ALAGAPPA UNIVERSITY

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(A State University Established by the Government of Tamilnadu)
KARAIKUDI – 630 003

DIRECTORATE OF DISTANCE EDUCATION

M. Sc.,

III - SEMESTER

34434

PRACTICAL: INORGANIC CHEMISTRY

SYLLABI-BOOK MAPPING TABLE
PRACTICAL: INORGANIC CHEMISTRY

INTRODUCTION

Quantitative analysis is the determination of the absolute or relative abundance (in concentration) of one, several or all particular substances present in a sample. For example, chemists might want to know the exact composition of some new compound that has been discovered. Both of these questions can be answered by the procedures of quantitative analysis. Quantitative techniques can be divided into two general categories: wet or classical techniques and instrumental methods.

OBJECTIVES

After reading this unit you will be able to:

➢ Maintain a laboratory notebook.

➢ Have knowledge of commonly used apparatus in the laboratory.

➢ Know the method of using a pipette, burette, volumetric flask and analytical balance.

➢ Explain different terms like precipitation, digestion, filtration and ignition, drying, cooling etc.

➢ Describe the process of titration.
➢ Classify the titration.

➢ Classify the indicator.

➢ Determine the strength of given sodium hydroxide (NaOH) solution.

➢ Have knowledge of lab reagents.
➢ Know the safety measures taken in the laboratory.

Classical methods

Classical methods have been used since the beginning of modern chemistry in the nineteenth century. They generally make use of balances and calibrated glass containers to measure the percentage composition of a compound or mixture. For example, the procedure known as gravimetric analysis involves the addition of some chemical to the unknown compound or mixture to produce a precipitate. A precipitate is a solid formed during a chemical reaction—usually in water—that eventually settles out of the solution. In a gravimetric analysis, the precipitate is filtered, washed, dried, and weighed. The composition of the original unknown can then be calculated from the weights of the precipitate and sample and original unknown. Precipitation methods are the most important gravimetric methods. Limitations of gravimetric methods include the requirement that the precipitated component has an extremely low solubility. The precipitate must also be of high purity and be easily filterable.

Another classical form of quantitative analysis is known as volumetric analysis. Volumetric analysis uses a procedure known as titration, in which a solution whose concentration is known precisely is caused to react with an unknown sample. The amount of the known solution needed to react precisely with the sample of the unknown can be used to calculate the percentage composition of the unknown. When

titrants composed of standard solutions are added to a sample that contains a component whose concentration is to be quantitatively determined, the method is referred to as a volumetric method. The component to be determined must react completely with the titrant in stoichiometric proportions. From the volume of titrant required, the component's concentration is calculated. The implicity, quickness, and relatively low cost of volumetric methods make them the most widely used for the analysis of plating and related solutions.

This book, *Practical Inorganic Chemistry*, deals with the practical aspects of quantitative analysis of chemical compounds by Volumetric, Gravimetric and Complexometric analysis.

Gravimetric Methods of Analysis

A Gravimetric analysis is based upon the measurement of the weight of a substance that has a known composition and is chemically related to the analyte. There are two major types of gravimetric methods

Precipitation methods: In this method the analyte is converted to a sparingly soluble precipitate. This precipitate is then filtered, washed free of impurities, and converted to a product of known composition by suitable heat treatment, and the product is weighed.

Volatilization methods: In this the analyte or its decomposition products are volatilized at a suitable temperature. The volatile product is then collected and weighed, or, alternatively, the mass of the product is determined indirectly from the loss in mass of the sample.

PROPERTIES OF PRECIPITATES AND PRECIPITATING REAGENTS

A gravimetric precipitating agent should react specifically and selectively with the analyte. The ideal precipitating reagent would react with the analyte to give a product that is

1. Readily filtered and washed free of contaminants
2. Of sufficiently low solubility so that no significant loss of the solid occurs during filtration and washing
3. Unreactive with constituents of the atmosphere

Of known composition after it is dried or, if necessary, ignited

Particle Size and Filter ability of Precipitates

Precipitates made up of large particles are generally desirable in gravimetric work because large particles are easy to filter and wash free of impurities. In addition, such precipitates are usually purer than are precipitates made up of fine particles.

What Factors Determine Particle Size?

The particle size of solids formed by precipitation varies enormously. At one extreme are **colloidal suspension**, whose tiny particles are invisible to the naked eye (10^{-7} to 10^{-4} cm in diameter). Colloidal particles show no tendency to settle from solution, nor are they

easily filtered. At the other extreme are particles with dimensions on the order of tenths of millimeter or greater. The temporary dispersion of such particles in the liquid phase is called a **crystalline suspension**. The particles of a crystalline suspension tend to settle spontaneously and are readily filtered.

The particle size of a precipitate is influenced by experimental variables as precipitate solubility, temperature, reactant concentrations and the rate at which reactants are mixed. The particle size is related to a single property of the system called its **relative super saturation**, where relative supersaturation = $(Q - S) / S$

In this equation, Q is the concentration of the solute at any instant and S is its equilibrium solubility. When $(Q - S)/S$ is large, the precipitate tends to be colloidal. When $(Q - S) / S$ is small, a crystalline solid is more likely.

How do Precipitates form?

Precipitates form in two ways, by **nucleation** and by **particle growth**. The particle size of a freshly formed precipitate is determined by which way is faster. In nucleation, a few ions, atoms, or molecules (perhaps as few as four or five) come together to form a stable solid. Often, these nuclei form on the surface of suspended solid contaminants, such as dust particles. Further precipitation then involves a competition between additional nucleation and growth on existing nuclei (particle growth). If nucleation predominates, a precipitate containing a large number of small particles results; if growth predominates, a smaller number of larger particles is produced.

Controlling Particle Size

Experimental variables that minimize supersaturation and thus lead to crystalline precipitates include elevated temperatures to increase the solubility of the precipitate (S in Equation), dilute solutions (to minimize Q) and slow addition of the precipitating agent with good stirring. The last two measures also minimize the concentration of the solute (Q) at any given instant.

Larger particles can also be obtained by pH control, provided the solubility of the precipitate depends on pH.

Colloidal Precipitates

Coagulation of Colloids: Coagulation can be has tened by heating, stirring, and adding an electrolyte to the medium. Colloidal suspensions are stable because all the particles present are either positively or negatively charged. This charge results from cations or anions that are bound to the surface of the particles. The process by which ions are retained on the surface of a solid is known as adsorption. We can readily demonstrate that colloidal particles are charged by observing their migration when placed in an electrical field.

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Peptization of Colloids

Peptization refers to the process by which a coagulated colloid reverts to its original dispersed state. When a coagulated colloid is washed, some of the electrolyte responsible for its coagulation is leached from the internal liquid in contact with the solid particles. Removal of this electrolyte has the effect of increasing the volume of the counter-ion layer. The repulsive forces responsible for the original colloidal state are then reestablished, and particles detach themselves from the coagulated mass. The washings become cloudy as the freshly dispersed particles pass through the filter.

Crystalline Precipitates

Crystalline precipitates are generally more easily filtered and purified than coagulated colloids. In addition, the size of individual crystalline particles, and thus their filterability, can be controlled to a degree.

The particle size of crystalline solids can often be improved significantly by minimizing Q, maximizing S, or both in Equation. Minimization of Q is generally accomplished by using dilute solution and adding the precipitate from hot solution or by adjusting the pH of the precipitation medium.

Digestion of crystalline precipitates (without stirring) for some time after formation frequently yields a purer, more filterable product. The improvement in filterability results from the dissolution and recrystallization.

Co-precipitation

Co-precipitation is the phenomenon in which soluble compounds are removed from solution during precipitate formation. There are four types of co-precipitation:

i) surface adsorption, ii) mixed-crystal formation, iii) occlusion, iv) mechanical entrapment. Surface adsorption and mixed-crystal formation are equilibrium processes, whereas occlusion and mechanical entrapment arise from the kinetics of crystal growth.

Occlusion and Mechanical Entrapment

When a crystal is growing rapidly during precipitate formation, foreign ions in the counter-ion layer may become trapped or occluded within the growing crystal.

Mechanical entrapment occurs when crystals lie close together during growth. Both occlusion and mechanical entrapment are at a minimum when the rate of precipitate formation is low, that is, under conditions of low supersaturation. Digestion is often remarkably helpful in reducing these types of co-precipitation. The rapid solution and reprecipitation that goes on at the elevated temperature of digestion

opens up the pockets and allows the impurities to escape into the solution.

Precipitation from Homogeneous Solution

Precipitation from homogeneous solution is a technique in which a precipitating agent is generated in a solution of the analyte by a slow chemical reaction. Local reagent excesses do not occur because the precipitating agent appears gradually and homogeneously throughout the solution and reacts immediately with the analyte. As a result, the relative supersaturation is kept low during the entire precipitation. In general, homogeneously formed precipitates, both colloidal and crystalline, are better suited for analysis than a solid formed by direct addition of a precipitating reagent.

DRYING AND IGNITION OF PRECIPITATES

After filtration, a gravimetric precipitate is heated until its mass becomes constant. Heating removes the solvent and any volatile species carried down with the precipitate. Some precipitates are also ignited to decompose the solid and form a compound of known composition. This new compound is often called the weighing form.

The temperature required to produce a suitable weighing form varies from precipitate to precipitate.

Applications of Gravimetric Methods
- Extensive numbers of inorganic ions are determined with excellent precision and accuracy.
- Routine assays of metallurgical samples.
- Neutral species: water, SO_2, CO_2, I_2.
- Organic substances: lactose in milk products, salicylates in drug preparations, nicotine in pesticides, cholesterol in cereals,
- Relative precision 0.1 to 1%.
- Good accuracy

Disadvantages
- Careful and time consuming.
- Scrupulously clean glassware.
- Very accurate weighing.
- Co-precipitation.

BLOCK – I & II

Unit 1: Separation and estimation of Cu^{2+} - Ni^{2+} mixtures by volumetric method and the other by gravimetric method.

Introduction

Model metal is an alloy of nickel and copper which is highly resistant to corrosion. It is commonly used in applications involving exposure to acids.

Objectives

After studying and performing this experiment you should be able to separate and estimate the Cu^{2+} - Ni^{2+} mixtures by volumetric method and the other by gravimetric method.

Volumetric Estimation of Copper

Principle: Cu(II) reacts with KI giving a brown precipitate of Cu_2I_2 and liberating iodine. When an excess of KI is added to the solution containing Cu^{2+} in neutral or slightly acidic medium, quantitative liberation of iodine takes place.

$$2CuSO_4.5 H_2O + 4KI \longrightarrow 2CuI_2 + 2K_2SO_4 + 5H_2O$$

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

The liberating I_2 is titrated against thiosulphate which is previously standardized against std. $CuSO_4$ solution, equivalent Weight of Cu= 63.54

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

From the above equation it is evident that

$$2Cu^{2+} \equiv I_2 \equiv 2S_2O_3^{2-} \equiv 2e$$

The Equivalent weight of Cu^{2+} will be one half of twice the molecular involves two electrons per two moles of Cu^{2+}. Equivalent weight of $Cu^{2+} = (2 \times 63.5)/2 = 63.5$.

The titration fails when any mineral acid is present in the solution and therefore before commencing the titration the acid should be neutralized. This is done by dropwise addition of NH_4OH until a slight

blue precipitate just appears. The precipitate can be removed by addition of CH_3COOH in the solution

$$Cu(OH)_2 + 2CH_3COOH \longrightarrow Cu^{2+} + 2CH_3COO^- + 2H_2O$$

Moreover the precipitate of Cu_2I_2 absorbs I_2 from the solution and releases it slowly making the detection of sharp end point difficult. So, a small amount of NH_4SCN is added near the end point to displace the absorbed iodine from Cu_2I_2 precipitate

$$2NH_4OH + Cu^{2+} \longrightarrow 2NH_4^+ + Cu(OH)_2$$

<div align="right">Blue precipitate</div>

Calculation

Weight of $CuSO_4$	= 1.25 g
Strength of $CuSO_4$	$= \dfrac{1000 \times 1.25}{100 \times 249.68} = 0.05$ N

Titration-I: Standard $CuSO_4$ Vs Sodium thiosulphate. **Indicator: starch**

S. No.	Volume of $CuSO_4$ (mL)	Burette Readings (mL)		Volume of thio sulphate (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of $CuSO_4$	V_1 = 20 mL
Normality of $CuSO_4$	N_1 = 0.050 N
Volume of Sodium thiosulphate	V_2 =
Normality of Sodium thiosulphate	N_2 = ?
	$V_1N_1 = V_2N_2$
Strength of sodium thiosulphate	$N_2 = \dfrac{V_1 \times N_1}{V_2} = \dfrac{20 \times 0.05}{V_2} =$

Procedure

The thiosulphate is standardized by titrating against standard $CuSO_4$ for this 1.25g of $CuSO_4$ is weighed accurately and made up to a 100 mL SMF with few drops of con.H_2SO_4.

The given solution is made up into 250 mL SMF. Pipetted out 20 mL of solution in a 250 mL conical flask and neutralized the solution by drop wise addition of ammonium solution (1:1) until a blue precipitate appears. Redissolve the precipitate with minimum amount of acetic acid (CH_3COOH) and adding about 0.5 mLin excess. Dilute the solution to about 80 ml and add 10 ml of potassium iodide solution (10%). Keep the flask covered with watch glass in a dark and cool place for about 3–5

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minutes and titrate the liberated iodine with standard sodium thiosulphate solution from burette. When the colour of the solution fades to a light yellow, add 2 drops of starch followed by 2 ml of ammonium thiocyanate (NH_4SCN) solution (10%). Titrate the solution till the blue colour discharges and a white or flesh white residue is left in the flask. Repeat the titration to get concordant value.

Titration-II
Standard Sodium thiosulphate Vs given Copper Solution

Indicator: starch

S. No.	Volume of $CuSO_4$ (mL)	Burette Readings(mL)		Volume of thio sulphate (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of thiosulphate $\quad\quad\quad$ $V_1 =$ _____ mL
Normality of thiosulphate $\quad\quad\quad$ $N_1 =$
Volume of $CuSO_4$ $\quad\quad\quad\quad\quad\quad$ $V_2 = 20$ mL
Normality of $CuSO_4$ $\quad\quad\quad\quad\quad$ $N_2 = x$
Strength of $CuSO_4$ $\quad\quad\quad\quad\quad\quad$ $N_2 = \dfrac{V1 \times N1}{V2}$

$$= \frac{\text{volume of thio} \times \text{Normality of thio}}{V2}$$

The amount of Copper ions present in the whole of the given solution =

$$= \frac{\text{Normality of CuSO4(N2)} \times \text{Equivalent weight of copper} \times 250}{1000}$$

$$= \frac{N2 \times 63.54 \times 250}{1000} =$$

From this we can calculate the amount of copper ions present in the given solution.

Precipitate Gravimetric Estimation of Nickel

40 mL of the made up solution is pipetted out into a beaker. A few drops of dilute HCl(1:1) is added and heated. H_2S gas is passed for about 15 minutes till the precipitation is filtered through whatman 42 filter paper. The precipitate is washed with warm water and throughout. The solution is heated to expel the dissolved H_2S gas and the solution is

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concentrated to about 50 mL in hot condition a slight excess (20mL) of dimethyl glyoxime (1%)is added. Ammonia solution (1:1) is added drop wise with constant stirring until the precipitation is completed and slight excess of ammonia is added. It is digested and kept aside; completion of the precipitation is tested with drop of DMG in sintered crucible. The precipitation is tested with cold water until the filtrate is free from chloride. A duplicate experiment is also performed.

$$Ni^{2+} + 2 \quad \text{dimethyl glyoxime} \longrightarrow \text{Ni-DMG} + 2H^+$$

dimethyl glyoxime
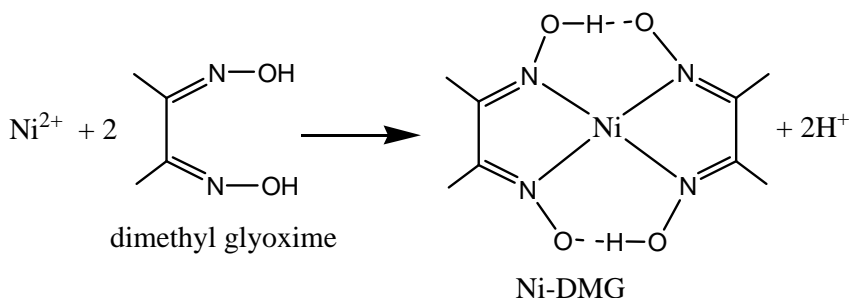
Ni-DMG

V Precipitative Gravimetric Estimation of Nickel

1	Empty Crucible weight (a)	
2	Weight of Precipitate+ Crucible (b)	
3	Weight of Precipitate (b-a)	

Calculation

288.69g of Ni-DMG complex contains 58.69 of nickel

-------- g of Ni-DMG complex contains $= \dfrac{58.69 \text{ X } (b-a)}{288.69} = A = $ _____

40mL of solution containing (A) _____ g of nickel

250mL of whole of the solution $= \dfrac{A \text{ X } 250}{40} = $

Result:

The amount of copper ions present in the whole of the given solution   =

The amount of nickel ions present in the whole of the given solution   =

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Unit 2: Separation and estimation of mixtures containing two components – 2 Separation and estimation of Cu^{2+}– Ba^{2+} mixtures by volumetric method and the other by gravimetric method.

Aim

To estimate the amount of copper by volumetrically and Barium by gravimetrically present in the whole of the given copper-barium solution.

Volumetric Estimation of Copper

Principle: Cu(II) reacts with KI giving a brown precipitate of Cu_2I_2 and liberating iodine. When an excess of KI is added to the solution containing Cu^{2+} in neutral or slightly acidic medium, quantitative liberation of iodine takes place.

$$2CuSO_4.5\,H_2O + 4KI \longrightarrow 2CuI_2 + 2K_2SO_4 + 5H_2O$$

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

The liberating I_2 is titrated against thiosulphate which is previously standardized against std. $CuSO_4$ solution, equivalent Weight of Cu= 63.54

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

From the above equation it is evident that

$$2Cu^{2+} \equiv I_2 \equiv 2S_2O_3^{2-} \equiv 2e$$

The Equivalent weight of Cu^{2+} will be one half of twice the molecular involves two electrons per two moles of Cu^{2+}. Equivalent weight of Cu^{2+} = (2 x 63.5)/2 = 63.5.

The titration fails when any mineral acid is present in the solution and therefore before commencing the titration the acid should be neutralized. This is done by dropwise addition of NH_4OH until a slight blue precipitate just appears.

The precipitate can be removed by addition of CH_3COOH in the solution

$$Cu(OH)_2 + 2CH_3COOH \longrightarrow Cu^{2+} + 2CH_3COO^- + 2H_2O$$

$$2NH_4OH + Cu^{2+} \longrightarrow 2NH_4^+ + Cu(OH)_2$$
$$\text{Blue precipitate}$$

Moreover the precipitate of Cu_2I_2 absorbs I_2 from the solution and releases it slowly making the detection of sharp end point difficult. So, a small amount of NH_4SCN is added near the end point to displace the absorbed iodine from Cu_2I_2 precipitate

Calculation

Weight of $CuSO_4$ = 1.25 g

Strength of $CuSO_4$ $= \dfrac{1000 \times 1.25}{100 \times 249.68}$ = 0.05 N

Titration-I: Standard $CuSO_4$ Vs Sodium thiosulphate. **Indicator: starch**

S. No.	Volume of $CuSO_4$ (mL)	Burette Readings (mL)		Volume of thio sulphate (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of $CuSO_4$ $\qquad$ V_1 = 20 mL
Normality of $CuSO_4$ $\qquad$ N_1 = 0.05 N
Volume of Sodium thiosulphate $\qquad$ V_2 =
Normality of Sodium thiosulphate $\qquad$ N_2 = ?

$$V_1N_1 = V_2N_2$$

Strength of sodium thiosulphate $\qquad$ $N_2 = \dfrac{V_1 \times N_1}{V_2} = \dfrac{20 \times 0.05}{V_2} =$

Procedure

The thiosulphate is standardized by titrating against standard $CuSO_4$ for this 1.25g of $CuSO_4$ is weighed accurately and made up to a 100 ml SMF with few drops of con.H_2SO_4.

The given solution is made up into 250 mL SMF. Pipetted out 20 mL of solution in a 250 ml conical flask and neutralized the solution by drop wise addition of ammonium solution (1:1) until a blue precipitate appears. Redissolve the precipitate with minimum amount of acetic acid (CH_3COOH) and adding about 0.5 mL in excess. Dilute the solution to about 80 mL and add 10 mL of potassium iodide solution (10%). Keep the flask covered with watch glass in a dark and cool place for about 3–5 minutes and titrate the liberated iodine with standard sodium thiosulphate

solution from burette. When the colour of the solution fades to a light yellow, add 2 drops of starch followed by 2 mL of ammonium thiocyanate (NH_4SCN) solution (10%). Titrate the solution till the blue colour disappears and a white or flesh white residue is left in the flask. Repeat the titration to get concordant value.

Titration-II

Standard Sodium thiosulphate Vs given Copper Solution.

Indicator: starch

S. No.	Volume of $CuSO_4$ (mL)	Burette Readings(mL)		Volume of thio sulphate (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of thiosulphate $V_1 = \_\_\_\_$ mL
Normality of thiosulphate $N_1 =$
Volume of $CuSO_4$ $V_2 = 20$ mL
Normality of $CuSO_4$ $N_2 = x$

Strength of $CuSO_4$ $N_2 = \dfrac{V_1 \times N_1}{V_2}$

$$= \frac{\text{volume of thio} \times \text{Normality of thio}}{V_2} =$$

The amount of Copper ions present in the whole of the given solution =

$$= \frac{\text{Normality of CuSO4(N2)} \times \text{Equivalent weight of copper} \times 250}{1000}$$

$$= \frac{N_2 \times 63.54 \times 250}{1000} =$$

The amount of copper ions present in the whole of the given solution=

Precipitative Gravimetric Estimation of Ba^{2+}ion:

Exactly 40 mL of the made up solution is pipetted out into clean conical flask and 2.5 ml of concentrated HCl was added. It was warmed to 60 °C and saturated with H_2S gas. The precipitate was filtered through a whatmann filter paper. The residue was washed with small amount of water. The washings were filtered and collected in a 400mL beaker. It was tested for completion of the precipitation and boiled off H_2S gas as well as reduce the volume of solution. The solution was neutralized with aqueous NH_3 to yellow after adding methyl red indicator.

About 5 g of NH_4Cl and 10 mL 1N acetic acid were added. Then excess of hot solution of potassium chromate was added with constant stirring. The precipitate was digested on water bath and tested for completion of precipitate. The precipitate filtered through weighed crucible and washed with hot water until free from chromate ion then it was dried to constant weight at 120ºC. A duplicate experiment is also performed.

$$BaCl_2 + K_2CrO_4 \longrightarrow 2KCl + BaCrO_4$$

Precipitative Gravimetric Estimation of Barium

1	Empty crucible weight (a)	
2	Weight of precipitate+ crucible (b)	
3	Weight of precipitate (b-a)	

Calculation

253.37g of barium chromate contains 137.36 of Ba^{2+}

-------- g of barium chromate Contains $= \dfrac{137.36 \times (b-a)}{253.36} = A =$

$=$_____ g barium

40 mL of solution containing (A) _____ g of barium

250 mL of whole of the solution $= \dfrac{A \times 250}{40} =$

The amount of barium ions present in the whole of the given solution=

Results

1. The amount of copper ions present in the whole of the given
 solution =

2. The amount of barium ions present in the whole of the given
 solution =

Separation and estimation
of mixtures containing
two components – 3

NOTES

Unit 3: Separation and estimation of mixtures containing two components – 3 Separation and estimation of Cu^{2+}– Zn^{2+} mixtures by volumetric method and the other by gravimetric method

Aim

To estimate the amount of copper by volumetrically and zinc by gravimetrically present in the whole of the given copper-zinc solution.

Volumetric Estimation of Copper

Principle

Cu(II) reacts with KI giving a brown precipitate of Cu_2I_2 and liberating iodine. When an excess of KI is added to the solution containing Cu^{2+} in neutral or slightly acidic medium, quantitative liberation of iodine takes place.

$$2CuSO_4.5\,H_2O + 4KI \longrightarrow 2CuI_2 + 2K_2SO_4 + 5H_2O$$

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$
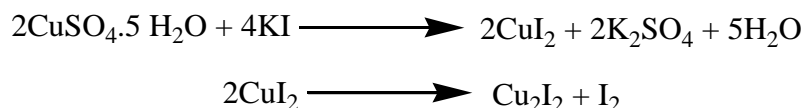
The liberating I_2 is treated against thiosulphate which is previously standardized against std. $CuSO_4$ solution, equivalent Weight of Cu= 63.54

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

From the above equation it is evident that

$$2Cu^{2+} \equiv I_2 \equiv 2S_2O_3^{2-} \equiv 2e$$

The Equivalent weight of Cu^{2+} will be one half of twice the molecular involves two electrons per two moles of Cu^{2+}. Equivalent weight of $Cu^{2+} = (2 \times 63.5)/2 = 63.5$.

The titration fails when any mineral acid is present in the solution and therefore before commencing the titration the acid should be neutralized. This is done by dropwise addition of NH_4OH until a slight blue precipitate just appears.

The precipitate can be removed by addition of CH_3COOH in the solution

$$2NH_4OH + Cu^{2+} \longrightarrow 2NH_4^+ + Cu(OH)_2$$

Blue precipitate

$$Cu(OH)_2 + 2CH_3COOH \longrightarrow Cu^{2+} + 2CH_3COO^- + 2H_2O$$

Moreover the precipitate of Cu_2I_2 absorbs I_2 from the solution and releases it slowly making the detection of sharp end point difficult. So, a small amount of NH_4SCN is added near the end point to displace the absorbed iodine from Cu_2I_2 precipitate

Calculation

Weight of $CuSO_4$ $= 1.25$ g

Strength of $CuSO_4$ $= \dfrac{1000 \times 1.25}{100 \times 249.68} = 0.05$ N

Titration-I: Standard $CuSO_4$ Vs Sodium thiosulphate. **Indicator: starch**

S. No.	Volume of $CuSO_4$ (mL)	Burette Readings (mL)		Volume of thio sulphate (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of $CuSO_4$ $V_1 = 20$ mL

Normality of $CuSO_4$ $N_1 = 0.050$ N

Volume of Sodium thiosulphate $V_2 =$

Normality of Sodium thiosulphate $N_2 = ?$

$$V_1N_1 = V_2N_2$$

Strength of sodium thiosulphate $N_2 = \dfrac{V_1 \times N_1}{V_2} = \dfrac{20 \times 0.05}{V_2} =$

Procedure

The thiosulphate is standardized by titrating against standard $CuSO_4$ for this 1.25 g of $CuSO_4$ is weighed accurately and made up to a 100 mL SMF with few drops of con.H_2SO_4.

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Separation and estimation
of mixtures containing
two components – 3

NOTES

The given solution is made up into 250 mL SMF. Pipetted out 20 mL of solution in a 250 mL conical flask and neutralized the solution by drop wise addition of ammonium solution (1:1) until a blue precipitate appears. Redissolve the precipitate with minimum amount of acetic acid (CH_3COOH) adding about 0.5 mL in excess. Dilute the solution to about 80 ml and add 10 mL of potassium iodide solution (10%). Keep the flask covered with watch glass in a dark and cool place for about 3–5 minutes and titrate the liberated iodine with standard sodium thiosulphate solution from burette. When the colour of the solution fades to a light yellow, add 2 drops of starch followed by 2 mL of ammonium thiocyanate (NH_4SCN) solution (10%).Titrate the solution till the blue colour disappears and a white or flesh white residue is left in the flask. Repeat the titration to get concordant value.

Titration-II

Standard sodium thiosulphate Vs given copper ion solution. **Indicator:starch**

S. No.	Volume of CuSO$_4$ (mL)	Burette Readings(mL)		Volume of thio sulphate (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of thiosulphate $\qquad$ $V_1 =$ _____ mL

Normality of thiosulphate $\qquad$ $N_1 =$

Volume of $CuSO_4$ $\qquad$ $V_2 = 20$ mL

Normality of $CuSO_4$ $\qquad$ $N_2 = x$

Strength of $CuSO_4$ $\qquad$ $N_2 = \dfrac{V1 \ X \ N1}{V2} =$

$$\dfrac{\text{volume of thio X Normality of thio}}{V2} =$$

The amount of Copper ions present in the whole of the given solution =

$$= \dfrac{\text{Normality of CuSO4(N2)X Equivalent weight of copper x 250}}{1000}$$

$$= \dfrac{N2 X \ 63.54 \ x \ 250}{1000} =$$

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Precipitative Gravimetric Estimation of Zinc

Oxine forms a sparingly soluble precipitate with zinc ion in acetic acid and ammonium acetate solution. It has the composition $Zinc(C_9H_6ON)_2$.Oxine is 8-hydroxy quinoline.

Procedure: 40ml of the made up solution pipetted out into a beaker. The solution is made slightly acidic by the addition of 5mL of dil. HCl. It is heated to boiling. HCl is added and heated. H_2S gas is passed for about 20 minutes. The precipitate is washed several times with water. The filtrate is then concentrated to about 50mL. The solution is made almost neutral by the addition of NH_3. About 5g of ammonium acetate and 4mL of acetic acid are added. The solution is warmed to 60°C. A slight excess of 2% solution of oxine (20mL) added by drop with stirring till the supernatant liquid is clear yellow in colour. It is then digested for about 2 minutes and filtered through a previously weighed G_4 Sintered crucible.The precipitate is washed several times with hot water. It is then dried in hot air oven at 130-140^{0}C and weighed. A duplicate experiment is also performed.

Precipitative Gravimetric Estimation of Zinc

1	Empty Crucible weight (a)	
2	Weight of Precipitate+ Crucible (b)	
3	Weight of Precipitate (b-a)	

Calculation:

353.69g of zinc Oxinate contains 63.37 of Zn^{2+}

-------- g of zinc Oxinate Contains $= \dfrac{63.37\ X\ (b-a)}{353.69} = A =$

A= _____ g Zinc

40 ml of solution containing (A) _____ g of zinc

250 ml of whole of the solution $= \dfrac{A\ X\ 250}{40} =$

The amount of zinc ions Present in the whole of the given solution=

Results

1. The amount of copper ions present in the whole of the given solution=

2. The amount of zinc ions present in the whole of the given solution=

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Separation and estimation
of mixtures containing
two components – 4

NOTES

Unit 4: Separation and estimation of mixtures containing two components – 4 Separation and estimation of Fe^{2+}– Ni^{2+} mixtures by volumetric method and the other by gravimetric method.

To estimate the amount of iron by volumetrically and nickel by gravimetrically in the whole of the given iron - nickel solution.

Volumetric Estimation of Iron

Principle:

The given ferric solution is reduced to the ferrous state using tin and hydrochloric acid. Tin (II) chloride formed on heating reduces iron(III) to iron(II).

$$2Fe^{3+} + Sn^{2+} \leftrightarrow 2Fe^{2+} + Sn^{4+}$$

Slight excess of $SnCl_2$ present is removed by the addition of $HgCl_2$ and a silky white Hg_2Cl_2 is obtained

$$2HgCl_2 + Sn^{2+} \rightarrow Hg_2Cl_2 + Sn^{4+} + 2Cl^-$$

The iron(II) solution thus obtained is reacted with acidified $K_2Cr_2O_7$ solution using diphenylamine as the internal indicator. The reaction is as follows.

$$Cr_2O_7{}^{2-} + 6Fe^{2+} + 14H^+ \leftrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Calculation

Weight of of iron (FAS)   = 3.92 g

Strength of FAS $= \dfrac{1000 \times 3.92}{100 \times 392}$ = 0.1 N

Titration-I: Standardisation of $K_2Cr_2O_7$ Vs FAS.

$K_2Cr_2O_7$ Vs FAS   .   **Indicator: Diphenylamine**

S. No.	Volume of FAS (mL)	Burette Readings (mL)		Volume of $K_2Cr_2O_7$ (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of FAS	V_1	$= 20$ mL
Strength of FAS	N_1	$= 0.1$ N
Volume of $K_2Cr_2O_7$	V_2	$=$
Normality of $K_2Cr_2O_7$	N_2	$= ?$
	$V_1N_1 = V_2N_2$	
Strength of $K_2Cr_2O_7$	$N_2 = \dfrac{V1 \text{ X } N1}{V2} = \dfrac{20 \text{ X } 0.1}{V2} =$	

Procedure:

The given solution is made up into a 250mL standard flask. 20mL of this solution is pipetted out into a beaker. It is heated and to the hot solution 2 drops of Con.HCl is added followed by concentrated tin(II) chloride in drops with stirring until the yellow colour disappears. Then dil.HCl is added till the solution becomes green. The solution is then rapidly cooled under the tap. A slight excess of stannous chloride present is removed by adding 10mL of a saturated solution of mercuric chloride rapidly in one portion with through mixing. A silky white precipitate of mercurous chloride is obtained, if a grey or black precipitate is obtained it has to be thrown out. To the resulting solution about 5mL of syrupy phosphoric acid and 2 drops of diphenylamine indicator are added and titrated against the standard dichromate solution. The solution first becomes straw yellow, greenish and dark green. The end point is the permanent appearance of blue – violet colour. The titration is repeated for concordant values.

Standard $K_2Cr_2O_7$ solution is prepared by weighing accurately about 1.25g of analar $K_2Cr_2O_7$ and making up in 250mL standard flask. Equivalent weight of $K_2Cr_2O_7 = 49$.

Titration-II

Standard $K_2Cr_2O_7$ Vs given unknown iron solution. **Indicator: Diphenyl Amine**

S. No.	Volume of unknown iron solution (mL)	Burette Readings (mL)		Volume of $K_2Cr_2O_7$ (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of $K_2Cr_2O_7$	$V_1 = \underline{\quad}$ mL
Normality of $K_2Cr_2O_7$	$N_1 =$

Separation and estimation
of mixtures containing
two components – 4

Volume of given unknown iron solution $V_2 = 20$ mL

Normality of given unknown iron solution $N_2 = x$

Strength of given unknown iron solution $N_2 = \dfrac{V_1 \times N_1}{V_2} =$

$$= \frac{\text{volume of K2Cr2O7} \times \text{Normality of K2Cr2O7}}{V_2} =$$

The amount of iron ions present in the whole of the given solution =

$$= \frac{\text{Strength of given unknown iron solution}(N2) \times \text{Equivalent weight of iron} \times 250}{1000}$$

$$= \frac{N2 \times 55.84 \times 250}{1000} =$$

The amount of iron ions present in the whole of the given solution=

Precipitative Gravimetric Estimation of Nickel

40 mL of the made up solution is pipetted out into a beaker. A few drops of dilute HCl(1:1) is added and heated. H_2S gas is passed for about 15 minutes till the precipitation is filtered through whatmann 42 filter paper. The precipitate is washed with warm water and throughout. The solution is heated to expel the dissolved H_2S gas and the solution is concentrated to about 50 mL in hot condition a slight excess(20mL) of dimethyl glyoxime (1%) is added. Ammonia solution (1:1) is added drop wise with constant stirring until the precipitation is completed and slight excess of ammonia is added. It is digested and kept aside; completion of the precipitation is tested with drop of DMG in sintered crucible. The precipitate is washed with cold water until the filtrate is free from chloride. It is then dried in hot air oven at $130 - 140^{o}$C and weighed. A duplicate experiment is also performed.

dimethyl glyoxime

Ni-DMG

Precipitative Gravimetric Estimation of Nickel

1	Empty crucible weight (a)	
2	Weight of precipitate+ crucible (b)	
3	Weight of precipitate (b-a)	

Calculation:

288.69g of Ni-DMG Complex contains 58.69 of Nickel

-------- g of Ni-DMG Complex Contains $= \dfrac{58.69 \text{ X } (b-a)}{288.69} = A =$

$= \underline{\hspace{1cm}} \quad g$

40mL of solution containing (A) _____ g of nickel

250mL of whole of the solution $= \dfrac{A \text{ X } 250}{40} =$

The amount of nickel ions present in the whole of the given
solution   =

Result:

The amount of Iron ions present in the whole of the given
solution =

The amount of nickel ions present in the whole of the given
solution =

Unit 5: Separation and estimation of mixtures containing two components – 5

Separation and estimation of Fe^{2+}– Zn^{2+} mixtures by volumetric method and the other by gravimetric method

Aim:

To estimate the amount of iron by volumetrically and zinc by gravimetrically in the whole of the given iron - zinc solution.

Volumetric Estimation of Iron

Principle:

The given ferric solution is reduced to the ferrous state using tin and hydrochloric acid. Tin (II) chloride formed on heating reduces iron(III) to iron(II).

$$2Fe^{3+} + Sn^{2+} \leftrightarrow 2Fe^{2+} + Sn^{4+}$$

Slight excess of $SnCl_2$ present is removed by the addition of $HgCl_2$ and a silky white $HgCl_2$ is obtained

$$2HgCl_2 + Sn^{2+} \rightarrow Hg_2Cl_2 + Sn^{4+} + 2Cl^-$$

The iron(II) solution thus obtained is reacted with acidified $K_2Cr_2O_7$ solution using diphenylamine as the internal indicator. The reaction is as follows.

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \leftrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Calculation

Weight of of iron (FAS)	= 3.92 g
Strength of FAS	$= \dfrac{1000 \times 3.92}{100 \times 392}$ = 0.1 N

Titration-I: Standardisation of $K_2Cr_2O_7$ Vs FAS.

$K_2Cr_2O_7$ Vs FAS.　　　　　　　　**Indicator: diphenylamine**

S. No.	Volume of FAS (mL)	Burette Readings (mL)		Volume of $K_2Cr_2O_7$ (mL)
		Initial	Final	
1	20	0		

2	20	0			

Volume of FAS

$$V_1 = 20 \text{ mL}$$

Strength of FAS $\quad N_1 = 0.1 \text{ N}$

Volume of $K_2Cr_2O_7$ $\quad V_2 =$

Normality of $K_2Cr_2O_7$ $\quad N_2 = ?$

$$V_1N_1 = V_2N_2$$

Strength of $K_2Cr_2O_7$ $\quad N_2 = \dfrac{V1 \times N1}{V2} = \dfrac{20 \times 0.1}{V2} =$

Procedure

The given solution is made up in a 250mL standard flask. 20mL of this solution is pipetted out into a beaker. It is heated and to the hot solution 2 drops of Con. HCl is added followed by concentrated tin(II) chloride in drops with stirring until the yellow colour disappears. Then dil. HCl is added till the solution becomes green. The solution is then rapidly cooled under the tap. A slight excess of stannous chloride present is removed by adding 10mL of a saturated solution of mercuric chloride rapidly in one portion with through mixing. A silky white precipitate of mercurous chloride is obtained, if a grey or black precipitate is obtained it has to be thrown out. To the resulting solution about 5mL of syrupy phosphoric acid and 2 drops of diphenylamine indicator are added and titrated against the standard dichromate solution. The solution first becomes straw yellow, greenish and dark green. The end point is the permanent appearance of blue – violet colour. The titration is repeated for concordant values.

Standard $K_2Cr_2O_7$ solution is prepared by weighing accurately about 1.25g of analar $K_2Cr_2O_7$ and making up in 250ml standard flask. Equivalent weight of $K_2Cr_2O_7 = 49$.

Titration-II

Standard $K_2Cr_2O_7$ Vs given unknown iron solution.
Indicator: Diphenyl Amine

S. No.	Volume of unknown iron solution (mL)	Burette Readings(mL)		Volume of $K_2Cr_2O_7$ (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of $K_2Cr_2O_7$ $\quad V_1 = \underline{\quad\quad} \text{ mL}$

Normality of $K_2Cr_2O_7$ $\qquad$ $N_1 =$

Volume of given unknown iron solution $\qquad$ $V_2 = 20 \text{ mL}$

Normality of given unknown iron solution $\qquad$ $N_2 = x$

Strength of given unknown iron solution $\qquad$ $N_2 = \dfrac{V_1 \times N_1}{V_2} =$

$$= \dfrac{\text{volume of K2Cr2O7 X Normality of K2Cr2O7}}{V_2} =$$

The amount of iron ions present in the whole of the given solution =

$$= \dfrac{\text{Strength of given unknown iron solution(N2) X Equivalent weight of iron x 250}}{1000}$$

$$= \dfrac{N_2 \times 55.84 \times 250}{1000} =$$

The amount of iron ions present in the whole of the given
solution =

Precipitative Gravimetric Estimation of Zinc

Oxine forms a sparingly soluble precipitate with zinc ion in acetic acid and ammonium acetate solution. It has the composition zinc$(C_9H_6ON)_2$.Oxine is 8-hydroxy quinoline.

Procedure: 40mLof the made up solution pipetted out into a beaker.The solution is made slightly acidic by the addition of 5ml of dil. HCl. It is heated to boiling. HCl is added and heated. H_2S gas is passed for about 20 minutes. The precipitate is washed several times with water. The filtrate is then concentrated to about 50mL.The solution is made almost neutral by the addition of NH_3. About 5g of ammonium acetate and 4mL of acetic acid are added. The solution is warmed to 60°C. A slight excess of 2% solution of oxine (20mL) added by drop with stirring till the supernatant liquid is clear yellow in colour. It is then digested for about 2 minutes and filtered through a previously weighed G_4 Sintered crucible. The precipitate is washed several times with hot water. It is then dried in a hot air oven at 130-140^{0}C and weighed. A duplicate experiment is also performed.
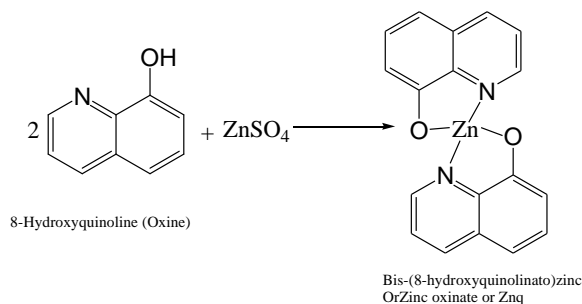
8-Hydroxyquinoline (Oxine)

Bis-(8-hydroxyquinolinato)zinc
OrZinc oxinate or Znq

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Precipitative Gravimetric Estimation of Zinc

1	Empty crucible weight (a)	
2	Weight of precipitate+ crucible (b)	
3	Weight of precipitate (b-a)	

Calculation

353.69g of Zinc Oxinate contains 63.37 of Zn^{2+}

-------- g of Zinc Oxinate contains $= \dfrac{63.37 \text{ X (b}-\text{a)}}{353.69} = A =$

$$A = \underline{\qquad} \text{ g}$$

40 mL of solution containing (A) _____ g of zinc

250 mL of whole of the solution $= \dfrac{A \text{ X } 250}{20} =$

The amount of zinc ions present in the whole of the given solution =

Results

1. The amount of iron ions present in the whole of the given solution =

2. The amount of zinc ions present in the whole of the given
 solution =

Unit 6: Separation and estimation of mixtures containing two components – 6

Separation and estimation of Fe^{2+}-Ba^{2+} mixtures by volumetric method and the other by gravimetric method

Aim:

To estimate the amount of iron by volumetrically and Barium by gravimetrically in the whole of the given iron - barium solution.

Volumetric Estimation of Iron

Principle:

The given ferric solution is reduced to the ferrous state using tin and hydrochloric acid. Tin (II) chloride formed on heating reduces iron(III) to iron(II).

$$2Fe^{3+} + Sn^{2+} \leftrightarrow 2Fe^{2+} + Sn^{4+}$$
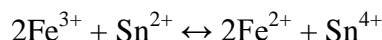
Slight excess of $SnCl_2$ present is removed by the addition of $HgCl_2$ when a silky white Hg_2Cl_2 is obtained

$$2HgCl_2 + Sn^{2+} \rightarrow Hg_2Cl_2 + Sn^{4+} + 2Cl^-$$

The iron(II) solution thus obtained is reacted with acidified $K_2Cr_2O_7$ solution using diphenylamine as the internal indicator. The reaction is as follows.

$$Cr_2O_7{}^{2-} + 6Fe^{2+} + 14H^+ \leftrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Calculation

Weight of of iron (FAS)	$= 3.92$ g	
Strength of FAS	$= \dfrac{1000 \times 3.92}{100 \times 392}$	$= 0.1$ N

Titration-I: Standardisation of $K_2Cr_2O_7$ Vs FAS.

$K_2Cr_2O_7$ Vs FAS.   **Indicator: diphenylamine**

S. No.	Volume of FAS (mL)	Burette Readings (mL)		Volume of $K_2Cr_2O_7$ (mL)
		Initial	Final	
1	20	0		

	2	20	0			

Volume of FAS

$$V_1 = 20 \text{ mL}$$

Strength of FAS $\qquad N_1 = 0.1 \text{ N}$

Volume of $K_2Cr_2O_7$ $\qquad V_2 =$

Normality of $K_2Cr_2O_7$ $\qquad N_2 = ?$

$$V_1N_1 = V_2N_2$$

Strength of $K_2Cr_2O_7$ $\qquad N_2 = \dfrac{V_1 \times N_1}{V_2} = \dfrac{20 \times 0.1}{V_2} =$

Procedure

     The given solution is made up in a 250mL standard flask. 20mL of this solution is pipetted out into a beaker. It is heated and to the hot solution 2 drops of Con.HCl is added followed by concentrated tin(II) chloride in drops with stirring until the yellow colour disappears. Then dil.HCl is added till the solution becomes green. The solution is then rapidly cooled under the tap. A slight excess of stannous chloride present is removed by adding 10mL of a saturated solution of mercuric chloride rapidly in one portion with through mixing. A silky white precipitate of mercurous chloride is obtained, if a grey or black precipitate is obtained, it has to be thrown out. To the resulting solution about 5mL of syrupy phosphoric acid and 2 drops of diphenylamine indicator are added and titrated against the standard dichromate solution. The solution first becomes straw yellow, greenish and dark green. The end point is the permanent appearance of blue-violet colour. The titration is repeated for concordant values.

     Standard $K_2Cr_2O_7$ solution is prepared by weighing accurately about 1.25g of analar $K_2Cr_2O_7$ and making up in 250mL standard flask. Equivalent weight of $K_2Cr_2O_7$ = 49.

Titration-II

Standard $K_2Cr_2O_7$ Vs given unknown iron solution.

Indicator: Diphenyl Amine

S. No.	Volume of unknown iron solution (mL)	Burette Readings (mL)		Volume of $K_2Cr_2O_7$ (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of $K_2Cr_2O_7$ $\qquad V_1 = \underline{\quad\quad}$ mL

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Normality of $K_2Cr_2O_7$ $\qquad$ $N_1 =$

Volume of given unknown iron solution $\qquad$ $V_2 = 20$ mL

Normality of given unknown iron solution $\quad$ $N_2 = x$

Strength of given unknown iron solution $\qquad$ $N_2 = \dfrac{V_1 \times N_1}{V_2} =$

$$= \dfrac{\text{volume of K2Cr2O7} \times \text{Normality of K2Cr2O7}}{V_2} =$$

The amount of iron ions present in the whole of the given solution =

$$= \dfrac{\text{Strength of given unknown iron solution(N2)} \times \text{Equivalent weight of iron} \times 250}{1000}$$

$$= \dfrac{N2 \times 55.84 \times 250}{1000} =$$

The amount of iron ions present in the whole of the given solution=

Precipitative Gravimetric Estimation of Ba^{2+} ion:

Exactly 40 mL of the made up solution is pipetted out into clean conical flask and 2.5 mL of concentrated HCl was added. It was warmed to 60 °C and saturated with H_2S gas. The precipitate was filtered through a whatmann filter paper. The residue was washed with small amount of water. The washings were filtered and collected in a 400mL beaker. It was tested for completion of the precipitation and boiled off H_2S gas as well as to reduce the volume of solution. The solution was neutralized with aqueous NH_3 to yellow after adding methyl red indicator.

About 5 g of NH_4Cl and 10 mL 1N acetic acid were added. Then excess of hot solution of potassium chromate was added with constant stirring. The precipitate was digested on water bath and tested for completion of precipitate. The precipitate filtered through weighed crucible and washed with hot water until free from chromate ion then it was dried to constant weight at 120 ºC. A duplicate experiment is also performed.

$$BaCl_2 + K_2CrO_4 \longrightarrow 2KCl + BaCrO_4$$

Precipitative Gravimetric Estimation of Barium

1	Empty crucible weight (a)	
2	Weight of precipitate+ crucible (b)	
3	Weight of precipitate (b-a)	

Calculation:

253.37g of barium chromate contains 137.36 of Ba^{2+}

-------- g of barium chromate Contains $= \frac{137.36 \text{ X } (b-a)}{253.36} = A =$

$=$_____ g barium

40 mL of solution containing (A) _____ g of barium

250 mL of whole of the solution $= \frac{A \text{ X } 250}{40} =$

The amount of barium ions present in the whole of the given solution =

Results

1. The amount of Iron ions present in the whole of the given solution =

2. The amount of barium ions present in the whole of the given solution =

Complexometric
estimation of binary
mixture of cations-

Block-3: Complexometric estimation of binary mixture of cations -1

Introduction

Complexometric titration is a type of titration based on complex formation between the analyte and titrant. Complexometric titrations are particularly useful for determination of a mixture of different metal ions in solution. An indicator with a marked color change is usually used to detect the end-point of the titration. Any complexation reaction can in theory be applied as a volumetric technique provided that

　　　• the reaction reaches equilibrium rapidly following each addition of titrant.

　　　• interfering situations do not arise (such as stepwise formation of various complexes resulting in the presence of more than one complex in solution in significant concentration during the titration process).

　　　• complexometric indicator capable of locating equivalence point with fair accuracy is available

Complexometric titration with EDTA

　　　Ethylenediamminetetraaceticacid, has four carboxyl groups and two amine groups that can act as electron pair donors, or Lewis bases. The ability of EDTA to potentially donate its six lone pairs of electrons for the formation of coordinate covalent bonds to metal cations makes EDTA a hexadentate ligand. However, in practice EDTA is usually only partially ionized, and thus forms fewer than six coordinate covalent bonds with metal cations. Disodium EDTA, commonly used in the standardization of aqueous solutions of transition metal cations, only forms four coordinate covalent bonds to metal cations at pH values less than or equal to 12 as in this range of pH values the amine groups remain protonated and thus unable to donate electrons to the formation of coordinate covalent bonds.

　　　In analytical chemistry the shorthand "Na_2H_2Y" is typically used to designate disodium EDTA. This shorthand can be used to designate any species of EDTA. The "Y" stands for the EDTA molecule, and the "Hn" designates the number of acidic protons bonded to the EDTA molecule. EDTA forms an octahedral complex with most 2+ metal cations, M^{2+}, in aqueous solution. The main reason that EDTA is used so extensively in the standardization of metal cation solutions is that the formation constant for most metal cation- EDTA complexes is very high, meaning that the equilibrium for the reaction :EDTA is assigned the formula H_4Y: the dissolution salt is therefore Na_2H_2Y and affords the complex-forming ion H_2Y^{2-} in aqueous solution; it reacts with all metals in 1:1 ratio. The reactions with cations, e.g. M^{2+}, may be written as:

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$$M^{2+} + H_2Y^{2-} \rightleftharpoons MY^{2-} + 2H^+ \qquad (1)$$
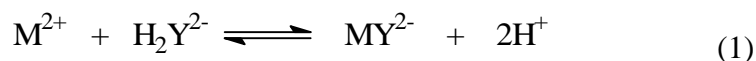
For other cations, the reactions may be expressed as:

$$M^{3+} + H_2Y^{2-} \rightleftharpoons MY^- + 2H^+ \qquad (2)$$

$$M^{4+} + H_2Y^{2-} \rightleftharpoons MY + 2H^+ \qquad (3)$$

$$\text{or } M^{n+} + H_2Y^{2-} \rightleftharpoons (MY)^{(n-4)+} + 2H^+ \qquad (4)$$
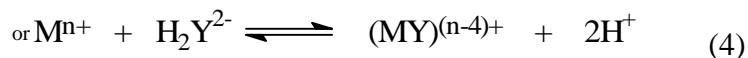
One mole of the complex-forming H_2Y^{2-} reacts in all cases with one mole of the metal ion and in each case, also, two moles of hydrogen ions are formed. It is apparent from equation (4) that the dissociation of the complex will be governed by the pH of the solution; lowering the pH will decrease stability of the metal-EDTA complex. The more stable the complex, the lower the pH at which an EDTA titration of the metal ion in question may be carried out. Table indicates minimum pH values for the existence of EDTA complexes of some selected metals.

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

Minimum pH at which complexes exist	Selected metals
1-3	Zr^{4+}; Hf^{4+}; Th^{4+}; Bi^{3+}; Fe^{3+}
4-6	Pb^{2+}; Cu^{2+}; Zn^{2+}; Co^{2+}; Ni^{2+}, Mn^{2+}; Fe^{2+}; Al^{3+}; Cd^{2+}; Sn^{2+}
8-10	Ca^{2+}; Sr^{2+}; Ba^{2+}; Mg^{2+}

It is thus seen that, in general, EDTA complexes with metal ions of the charge number 2 are stable in alkaline or slightly acidic solution, whilst complexes with ions of charge numbers 3 or 4 may exist in solutions of much higher acidity.

To carry out metal cation titrations using EDTA it is almost always necessary to use a complexometric indicator, usually an organic dye such as Fast Sulphon Black, Eriochrome Black T, Eriochrome Red B or Murexide, to determine when the end point has been reached. These dyes bind to the metal cations in solution to form colored complexes. However, since EDTA binds to metal cations much more strongly than does the dye used as an indicator the EDTA will displace the dye from the metal cations as it is added to the solution of analyte. A color change in the solution being titrated indicates that all of the dye has been displaced from the metal cations in solution, and that the end point has been reached.

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Complexometric
estimation of binary
mixture of cations-

NOTES
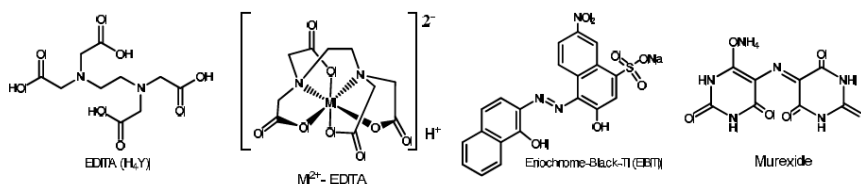
Structure of EDTA, Metal-EDTA, Eriochrome black –T and Murexide

EDTA TITRATION CURVES

If, in the titration of a strong acid, pH is plotted against the volume of the solution of the strong base added, a point of inflexion occurs at the equivalence point. Similarly, in the EDTA titration, if pM (negative logarithm of the 'free' metal ion concentration: $pM = - \log [M^{n+}]$) is plotted against the volume of EDTA solution added, a point of inflexion occurs at the equivalence point; in some instances this sudden increase may exceed 10 pM units. The general shape of titration curves obtained by titrating 10.0 mL of a 0.01 M solution of a metal ion M with a 0.01 M EDTA solution is shown in Figure 3. The apparent stability constants of various metal-EDTA complexes are indicated at the extreme right of the curve. It is evident that the greater the stability constant, the sharper is the end point provided the pH is maintained constant.
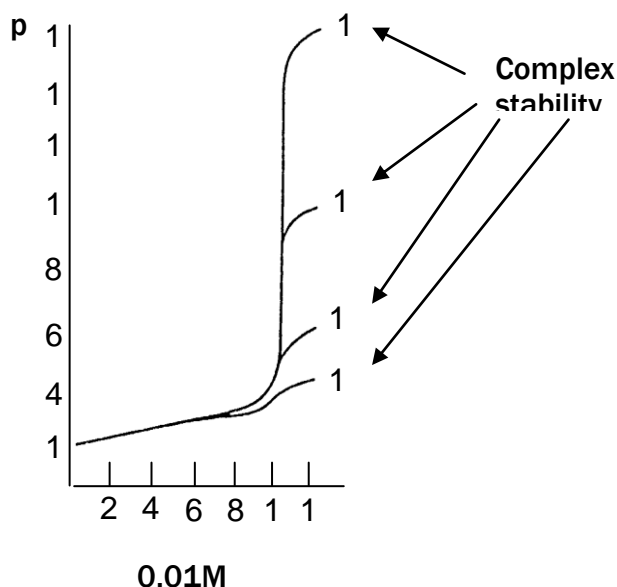
EDTA titration curves and the effect of K_{st} (complex stability constant).

Titration curves for 0.1 M Ca^{2+} versus 0.1 M EDTA at pH 7 and pH 10 are shown in Figure 4. This figure indicates the effect of pH on apparent stability constants and correspondingly on the shape of the titration curve.
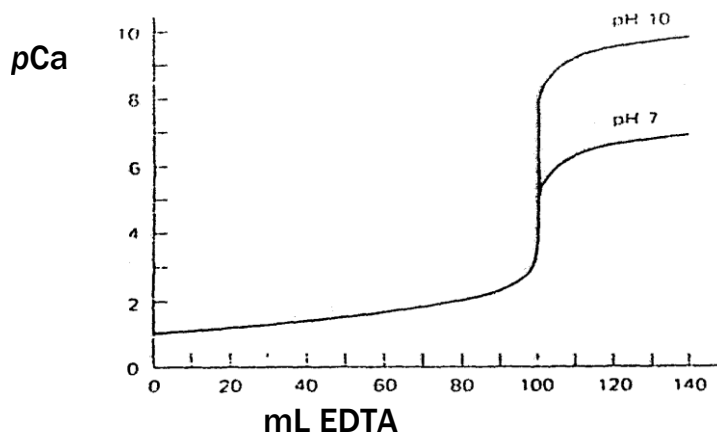
Titration curves of Ca^{2+} with EDTA at pH 7 and pH 10.

METAL ION INDICATORS (METALLOCHROMIC INDICATORS):

Several methods can be used to detect the end point in EDTA titrations. The most common technique is to use a metal ion indicator. A metal ion indicator is a compound whose color changes when it binds to a metal ion. Several common indicators are shown in Table 4. For an indicator to be useful, it must bind metal less strongly than EDTA does.

A typical analysis is illustrated by the titration of Mg^{2+} with EDTA using Eriochrome black T (EBT) as the indicator. We can write the reaction as follows:

$$\text{MgIn} + \text{EDTA} \rightarrow \text{MgEDTA} + \text{In}$$
$$\text{(red)} \quad \text{(colorless)} \quad \text{(colorless)} \quad \text{(blue)}$$
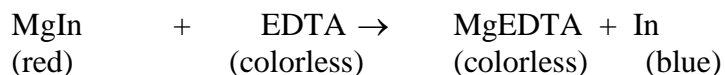
A small amount of indicator (In) is added to the Mg^{2+} to form a red complex. As EDTA is added, it reacts first with free, colorless Mg^{2+} and then with the small amount of red MgIn complex. (The EDTA must therefore bind to Mg^{2+} better than the indicator binds to Mg^{2+}). The change from the red of MgIn to the blue of unbound In indicates the end point of the titration.

Most metal ion indicators are also acid-base indicators. Because the color of free indicator is pH-dependent, most indicators can be used only in certain pH ranges. For example, xylenol orange (pronounced zyl-een-ol) changes from yellow to red when it binds to a metal ion at pH 5.5. This is an easy color change to observe. At pH 7.5 the change is from

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violet to red and rather difficult to see. A spectrophotometer can be used to measure an indicator color change, but it is more convenient if we can see it.

Common metal ion indicators, other than those mentioned in Table 4, are Eriochrome Blue-Black B, Patton and Reeders' indicator, Calcon, Calichrome, Fast Sulpone Black F, Catechol violet, Bromopyrogallol Red, Methylthymol Blue, Warianine Blue and Zincon.

Some metal ion indicators are unstable. Solutions of azo indicators (compounds with -N=N- bonds) deteriorate rapidly and should probably to prepared each week. Murexide solution should be prepared fresh each day.

INDICATOR BLOCKING:

For an indicator to be useful in the titration of a metal with EDTA, the indicator must give up its metal ion to the EDTA. If a metal does not freely dissociate from an indicator, the metal is said to block the indicator. Eriochrome black T is blocked by Cu^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, and Al^{3+}. It cannot be used as an indicator for the direct titration of any of these metals. Eriochrome black T can be used for a back titration, however, for example, excess standard EDTA can be added to Cu^{2+}. Then indicator is added and the excess EDTA is back-titrated with Mg^{2+}.

The success of an EDTA titration depends upon the precise determination of the end point. The most common procedure utilizes metal ion indicators. The requisites of a metal ion indicator for use in the visual detection of end points include:

(a) The color reaction must be such that before the end point, when nearly all the metal ions are complexed with EDTA, the solution is strongly colored.

(b) The color reaction should be specific or at least selective.

(c) The metal-indicator complex must possess sufficient stability, otherwise, because of dissociation, a sharp color change is not obtained. The metal-indicator complex must, however, be less stable than that the metal-EDTA complex to ensure that, at the end point, EDTA removes metal ions from the metal indicator-complex. The change in equilibrium from the metal-indicator complex to the metal-EDTA complex should be sharp and rapid.

(d) The color contrast between the free indicator and the metal-indicator complex should be readily observed.

(e) The indicator must be very sensitive to metal ions (i.e. to pM) so that the color change occurs as near to the equivalence point as possible.

(f) The above requirements must be fulfilled within the pH range at which the titration is performed.

A. Direct titration. The solution containing the metal ion to be determined is buffered to the desired pH (e.g. to pH = 10 with NH:-aq. NH,) and titrated directly with the standard EDTA solution. It may be

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necessary to prevent precipitation of the hydroxide of the metal (or a basic salt) by the addition of some auxiliary complexing agent, such as tartrate or citrate or triethanolamine. At the equivalence point the magnitude of the concentration of the metal ion being determined decreases abruptly. This is generally determined by the change in colour of a metal indicator or by amperometric, spectrophotometric, or potentiometric methods.

B. Back-titration. Many metals cannot, for various reasons, be titrated directly; thus they may precipitate from the solution in the pH range necessary for the titration, or they may form inert complexes, or a suitable metal indicator is not available. In such cases an excess of standard EDTA solution is added, the resulting solution is buffered to the desired pH, and the excess of the EDTA is back-titrated with a standard metal ion solution; a solution of zinc chloride or sulphate or of magnesium chloride or sulphate is often used for this purpose. The end point is detected with the aid of the metal indicator which responds to the zinc or magnesium ions introduced in the back-titration.

C. Replacement or substitution titration. Substitution titrations may be used for metal ions that do not react (or react unsatisfactorily) with a metal indicator, or for metal ions which form EDTA complexes that are more stable than those of other metals such as magnesium and calcium. The metal cation M^{n+} to be determined may be treated with the magnesium complex of EDTA, when the following reaction occurs:

$$M^{n+} + MgY^{2-} \rightleftharpoons (MY)^{(n-4)+} + Mg^{2+}$$
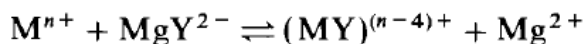
The amount of magnesium ion set free is equivalent to the cation present and can be titrated with a standard solution of EDTA and a suitable metal indicator. An interesting application is the titration of calcium. In the direct titration of calcium ions, solo chrome black gives a poor end point; if magnesium is present, it is displaced from its EDTA complex by calcium and an improved end point results

D. Alkalimetric titration: When a solution of disodium ethylenediaminetetraacetate, Na_2H_2Y, is added to a solution containing metallic ions, complexes are formed with the liberation of two equivalents of hydrogen ion: The hydrogen ions thus set free can be titrated with a standard solution of sodium hydroxide using an acid-base indicator or a potentiometric end point; alternatively, an iodate-iodide mixture is added as well as the EDTA solution and the liberated iodine is titrated with a standard thiosulphate solution. The solution of the metal to be determined must be accurately neutralized before titration; this is often a difficult matter on account of the hydrolysis of many salts, and constitutes a weak feature of alkali metric titration.

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TITRATION OF MIXTURES, SELECTIVITY, MASKING AND DEMASKING AGENTS

EDTA is a very unselective reagent because it complexes with numerous doubly, triply and quadruply charged cations. When a solution containing two cations which complex with EDTA is titrated without the addition of a complex-forming indicator, and if a titration error of 0.1 per cent is permissible, then the ratio of the stability constants of the EDTA complexes of the two metals M and N must be such that $K_M/K_N > 10^6$ if N is not to interfere with the titration of M. Strictly, of course, the constants K_M and K_N considered in the above expression should be the apparent stability constants of the complexes. If complex-forming indicators are used, then for a similar titration error $K_M/K_N > 10^8$. The following procedures will help to increase the selectivity:

(a) Suitable control of the pH of the solution.

This, of course, makes use of the different stabilities of metal-EDTA complexes. Thus bismuth and thorium can be titrated in an acidic solution (pH = 2) with xylenol orange or methylthymol blue as indicator and most divalent cations do not interfere. A mixture of bismuth and lead ions can be successfully titrated by first titrating the bismuth at pH 2 with xylenol orange as indicator, and then adding hexamine to raise the pH to about 5, and titrating the lead.

(b) Use of masking agents.

Masking may be defined as the process in which a substance, without physical separation of it or its reaction products, is so transformed that it does not enter into a particular reaction. Demasking is the process in which the masked substance regains its ability to enter into a particular reaction. By the use of masking agents, some of the cations in a mixture can often be 'masked' so that they can no longer react with EDTA or with the indicator. An effective masking agent is the cyanide ion; this forms stable cyanide complexes with the cations of Cd, Zn, Hg, Cu, Co, Ni, Ag, and the platinum metals, but not with the alkaline earths, manganese, and lead:

$$M^{2+} + 4CN^- \rightarrow [M(CN)_4]^{2-}$$
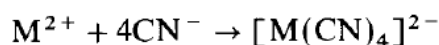
It is therefore possible to determine cations such as Ca^{2+}, Mg^{2+}, Pb^{2+}, and Mn^{2+} in the presence of the above-mentioned metals by masking with an excess of potassium or sodium cyanide. A small amount of iron may be masked by cyanide if it is first reduced to the iron(II) state by the addition of ascorbic acid. Titanium(IV), iron(III), and aluminium can be masked with triethanolamine; mercury with iodide ions; and aluminium, iron(III), titanium(IV), and tin(II) with ammonium fluoride (the cations of the alkaline-earth metals yield slightly soluble fluorides). Sometimes the metal may be transformed into a different oxidation state: thus copper(II) may be reduced in acid solution by hydroxylamine or

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ascorbic acid. After rendering ammoniacal, nickel or cobalt can be titrated using, for example, murexide as indicator without interference from the copper, which is now present as Cu(I). Iron(III) can often be similarly masked by reduction with ascorbic acid.

(c) Selective demasking.

The cyanide complexes of zinc and cadmium may be demasked with formaldehyde-acetic acid solution or, better, with chloral hydrate :

$$[Zn(CN)_4]^{2-} + 4H^+ + 4HCHO \rightarrow Zn^{2+} + 4HO \cdot CH_2 \cdot CN$$

The use of masking and selective demasking agents permits the successive titration of many metals. Thus a solution containing Mg, Zn, and Cu can be titrated as follows:

1. Add excess of standard EDTA and back-titrate with standard Mg solution using solochrome black as indicator. This gives the sum of all the metals present.

2. Treat an aliquot portion with excess of KCN (Poison !) and titrate as before. This gives Mg only.

3. Add excess of chloral hydrate (or of formaldehyde-acetic acid solution, (3:1) to the titrated solution in order to liberate the Zn from the cyanide complex, and titrate until the indicator turns blue. This gives the Zn only. The Cu content may then be found by difference.

Complexometric
estimation of binary
mixture of cations-1

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Unit 7: Complexometric estimation of binary mixture of cations -1
Estimation of Bi^{3+}- Pb^{2+} mixtures using EDTA as a complexing agent by adopting any one of the techniques, like precipitation, pH variation, masking and demasking.

To estimate the individual amount of bismuth and lead ions present in the whole of the given solution.

Principle:
The estimation was possible by making use of different stabilities of [Bi-EDTA] and [Pb-EDTA] complexes. Thus bismuth can be titrated in an acidic solution using xylenol orange (or) methyl thymal blue as indicator and most of the divalent cations do not interfere. After the estimation of bismuth, the pH of the solution is suitably raised to 5 to 6 units and then titrate the Lead.

Procedure

Titration-I
Standardization of EDTA using std. Lead Nitrate solution:
About 3.312 g of lead nitrate was weighed accurately in an electronic balance and dissolved in water and made upto100mL in a 100ml SMF. The solution was shaken well for uniform concentration. Exactly 20mL of the made up solution was pipetted out into a clean conical flask and diluted with 25ml of water. About 50mg of xylenol orange + KNO_3 mixture was added to it. Then the powdered hexamine was added to it slowly until the solution becomes an intense red colour (pH=6) the solution was titrated against EDTA solution taken in the burette. At the end point, colour change from pink to yellow. The titration was repeated to get concordant titre value.

Calculation

Weight of Lead Nitrate	= 3.312 g
Strength of Lead Nitrate	$= \frac{1000 \times 3.312}{100 \times 331.21} = 0.1$ N

Titration-I: Standardization of EDTA using std. Lead nitrate solution

Indicator: xylenol orange + KNO_3 mixture

S. No.	Volume of Lead nitrate (mL)	Burette Readings (mL)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of Lead nitrate $\qquad V_1 = 20$ mL

Normality of Lead nitrate $\qquad N_1 = 0.1$ N

Volume of EDTA $\qquad V_2 =$

Normality of EDTA $\qquad N_2 = ?$

$$V_1N_1 = V_2N_2$$

Strength of EDTA $\qquad N_2 = \dfrac{V_1 \times N_1}{V_2} = \dfrac{20 \times 0.1}{V_2} =$

Titration-II
Estimation of given solution
$\qquad$ The given solution is made up to 100mL in a 100mL SMF and the solution was shaken well for uniform concentration. Exactly 20mL of the solution was pipetted out into the conical flask. About 5mL of dil.HNO_3 was added to keep the pH of the solution in the range of 1-2 followed by 50mg xylenol orange + KNO_3 mixture. The solution was titrated against standardized EDTA taken in the burette. The end point was colour changed from red–purple to yellow.

$\qquad$ Add hexamine solution (10 % w/v) until the colour becomes red-purple, add 1-2 ml more. The titration was continued with the same EDTA solution until the colour changed from red to yellow. This gives the titre value for lead ion. Titration was repeated for concordant titre value.

Titration-II: Estimation of given solution
Indicator: xylenol orange + KNO_3 mixture

S. No.	Volume of Pb^{2+} & Bi^{3+} (mL)	Burette Readings (mL)		Volume of EDTA (mL)
		Initial	Final	
1				pH =1-2 for Bismuth
2				
3				pH= 6 for Lead
4				

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mixture of cations-1

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Estimation of Bi^{3+}

Volume of EDTA for Bi^{3+}	$V_1 =$
Normality of EDTA	$N_1 =$
Volume of Bi^{3+} solution	$V_2 = 20$ mL
Normality of Bi^{3+} solution	$N_2 =$

According to volumetric principle, $V_1 \times N_1 = V_2 \times N_2$

Normality of Bi^{3+} ion $N_2 = \dfrac{V1 \times N1}{20mL} =$

The amount of Bi^{3+} ions present in the whole of the given solution=

$=$

$\dfrac{\text{Strength of the given Bi3+solution (N2) X Equivalent weitght of Bismuth ion X 100}}{1000} =$

Titration-II
Estimation of Pb^{2+} ion

Volume of EDTA for Pb^{2+}	$V_1 =$
Normality of EDTA	$N_1 =$
Volume of Pb^{2+} ion	$V_2 = 20$ mL
Normality of Pb^{2+} ion	$N_2 =$
Normality of Pb^{2+} ion M_2	$= \dfrac{V1 \times M1}{20mL} =$

The amount of Pb^{2+} ion (in 100mL) =

$\dfrac{\text{Strength of the given Pb2+ ion solution (M2) X Equivalent weitght of lead ion X 100}}{1000} =$

The amount of lead(II) ions present in whole of the given solution $=$

Result:

1. The amount of bismuth(III) ions present in whole of the given
solution $=$
2. The amount of lead(II) ions present in whole of the given
solution $=$

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Unit 8: Complexometric estimation of binary mixture of cations -2

Estimation of Pb^{2+}– Ca^{2+} mixtures using EDTA as a complexing agent by adopting anyone of the techniques, like precipitation, pH variation, masking and demasking.

Aim

To estimate the individual amount of Ca^{2+} and Pb^{2+} ions present in whole of the given solution.

Procedure
Titration-I
Standardisation of EDTA using std. ZnO

About 0.10 g of ZnO was accurately weighed using electronic balance and dissolved in 2N HNO_3, made up in 100mL SMF. 20mL of this made up solution was pipetted out into a clean conical flask. The solution was diluted with 25mL of water. About 2mL of pH=10 buffer and two drops of Eriochrome black-T indicator were added. The end point was noted when the colour changed from wine red to blue colour. Titrations were repeated for concordant titre values.

STAGE-I

Preparation of Std. Zinc Oxide solution

Weight of Zinc Oxide   = 0.1 g

Normality of Zinc Oxide $= \dfrac{0.10 \times 1000}{100 \times 81.4} = 0.0122\ N$

TITRATION-I

Standardisation of EDTA using std. ZnO **Indicator:** Eriochrome black-T

S. No.	Volume of ZnO (mL)	Burette Readings (mL)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of Zinc Oxide V_1 = 20 mL

Normality of Zinc Oxide	$N_1 = 0.012$ N
Volume of EDTA	$V_2 =$
Normality of EDTA	$N_2 = ?$

$$V_1N_1 = V_2N_2$$

Strength of EDTA $\quad N_2 = \dfrac{V_1 \times N_1}{V_2} = \dfrac{20 \times 0.012}{V_2} =$

Titration-II

Estimation of both (Lead & Calcium) ions

The given solution was made up into 250mL SMF. Then 20mL of this solution was pipetted out into a clean conical flask. It was diluted to 50mL, and then 5mL of Eriochrome black-T indicator was also added. Then the solution was titrated against standardized EDTA taken in the burette. The end point was noted at the colour changes from wine red to blue. This value is the observed total value for both Pb^{2+} and Ca^{2+} ions.

TITRATION-II: Estimation of both Pb^{2+} & Ca^{2+} ions

Estimation of both Pb^{2+} & Ca^{2+} ions **Indicator:** Eriochrome black-T

S. No.	Volume of Pb^{2+} & Ca^{2+} ions (mL)	Burette Readings (mL)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

TITRATION-III: Estimation of Ca^{2+} ions only (Masking Method)

Titration-III

Estimation of Ca^{2+} ions only [Masking Method]

Exactly 20mL of the given made up solution was pipetted out into another conical flask. About 50mg of sodium diethyl dithiocarbomate was added to the solution to mask Pb^{2+} ions. Then 20mL of Std EDTA solution and 20mL of std. Zn^{2+} solution were added for back titration. Then 4mL of pH=10 buffer and two drops of EBT indicator were added. The excess of Zn^{2+} was titrated against standardized EDTA until the end point of colour changes from wine red to blue. This is the titre value only for Ca^{2+} ions. The titration was repeated for concordance.

$$Pb^{2+} \quad + \quad HY^{3-} \quad \xrightleftharpoons{pH = 10} \quad PbY^{2-} \quad + \quad HY^{3-}$$

analyte   excess known   metal ion-EDTA   unreacted
Colorless   amount (EDTA)   complex   EDTA
               colorless   (colorless)   (colorless

$$HY^{3-} \quad + \quad HIn^{2-} \quad + \quad Zn^{2+} \quad \xrightleftharpoons{pH = 10} \quad ZnY^{2-} \quad + \quad ZnY^{2-} \quad + \quad H^+$$

unreacted   Free indicator   titrant   metal ion-EDTA   metal ion-indicator
EDTA   complex   complex
(colorless)   (colorless)   (colorless)   (wine-red)

Estimation of Ca^{2+} ions   **Indicator:** Eriochrome black-T

S. No.	Volume of Ca^{2+}(mL)	Burette Readings (mL)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of EDTA required for Ca^{2+} ions only (x)   = (1 + 2) -3
Where

1 → Volume of EDTA added in titration –III for back titration
     = 20 mL

2 →Volume of EDTA required for titration – III for Ca^{2+} ions
only = _____   (Titration III burette Reading)

3 →Volume of EDTA required for titration – I for standardisation
 of ZnO   X =

ESTIMATION OF CALCIUM (II) IONS:

Volume of EDTA for Ca^{2+} V_1=

Normality of EDTA N_1 =

Volume of Ca^{2+} ions V_2= 20 mL

Normality of Ca^{2+} ion N_2= $\dfrac{V_1 \times N_1}{20mL}$=

The amount of Ca^{2+} ion present in the whole of the given solution =

$$\frac{\text{Strength of the Ca2+solution (N2) X Equivalent weitght of ca2+ ion X 250}}{1000} =$$

$$\frac{(N2) \times 40.07 \times 250}{1000} =$$

=

ESTIMATION OF LEAD (II) IONS:

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Volume of EDTA required for Pb^{2+} ions (Y) = 4 - x =

Where 4 → titration II end point

Calculation

Volume of EDTA for Pb^{2+} $\qquad\qquad\qquad$ $V_1=$

Normality of EDTA $\qquad\qquad\qquad\qquad$ $N_1 =$

Volume of Pb^{2+} ions $\qquad\qquad\qquad\qquad$ $V_2 = 20$ mL

Normality of Pb^{2+} ions $\qquad\qquad\qquad$ $N_2 = \dfrac{V_1 \times N_1}{20mL} =$

The amount of Pb^{2+} ion present in the whole of the given solution =

$$= \frac{\text{Strength of the Pb2+solution (N2) X Equivalent weitght of Pb2+ ion X 250}}{1000} =$$

$$\frac{\text{(N2) X 207.2 X 250}}{1000} =$$

Results:

1. The amount of Ca^{2+} ions present in whole of the given solution =
2. The amount of Pb^{2+} ions present in whole of the given solution =

Unit 9: Complexometric estimation of binary mixture of cations – 3

Estimation of Ni^{2+} – Cu^{2+} mixtures using EDTA as a complexing agent by adopting anyone of the techniques, like precipitation, pH variation, masking and demasking.

Aim

To estimate the individual amount of Ni^{2+} and Cu^{2+} ions present in whole of the given solution.

Principle:

The estimation is based on the reaction $Ni^{2+} + H_2 y^{2-} \rightarrow NiY^{2-} + 2H^+$. The end point is indicated by using mureoxide indicator. This indicator reacts with Ni^{2+}Ions to form a yellow colour. At the end point the Ni^{2+} ions react with EDTA to form metal EDTA complex and leave the free indicator which is bluish white in colour.

Cu(II) reacts with KI giving a brown precipitate of $CuCl_2$ and liberating iodine.

$2Cu+ + 4KI \rightarrow 4 K^+ + Cu_2I_2 + I_2$
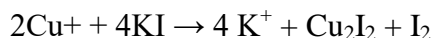
The liberated iodine is titrated against thiosulphate which is previously standardized against standard $CuSO_4$ solution.

Procedure
Titration-I
Standardisation of EDTA using Std. ZnO

About 0.10 g of ZnO was accurately weighed using electronic balance and dissolved in 2N HNO_3, made up in 100 mL SMF. 20mL of this made up solution was pipetted out into a clean conical flask. The solution was diluted with 25mL of water. About 2mL of pH=10 buffer and two drops of Eriochrome black-T indicator were added. The end point was noted when the colour changed from wine red to blue colour. Titrations were repeated for concordant titre values.

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STAGE-I

Preparation of std. Zinc Oxide solution

Weight of Zinc Oxide = 0.1 g

Normality of Zinc Oxide $= \dfrac{0.10 \times 1000}{100 \times 81.4} = 0.0122$ N

TITRATION-I

Standardisation of EDTA using std. ZnO **Indicator:** Eriochrome black-T

S. No.	Volume of ZnO (mL)	Burette Readings (ml)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of Zinc Oxide $\quad V_1 = 20$ mL

Normality of Zinc Oxide $\quad N_1 = 0.012$ N

Volume of EDTA $\quad V_2 =$

Normality of EDTA $\quad N_2 = ?$

$$V_1 N_1 = V_2 N_2$$

Strength of EDTA $\quad N_2 = \dfrac{V_1 \times N_1}{V_2} = \dfrac{20 \times 0.012}{V_2} =$

Titration II

The given solution is made upto 100mL in a standard measuring flask. 25 mLof the solution is pipetted out into a conical flask, diluted to 100mL with distilled water. 5-6 drops of freshly prepared mureoxide indicator is added followed by 10mL of 1M ammonium chloride solution. Concentrated solution of ammonium hydroxide is added drop wise until the pH is about 7, as shown by the yellow colour in the solution. The solution is titrated with 0.01 molar EDTA solution until the end point is reached.10mL of concentrated ammonia solution is added to make the solution strongly alkaline and titration is continued until the colour changes from yellow to bluish violet .Nickel complexes rather slowly ETDA , consequently the EDTA solution must be added drop wise near the end point. This titre value is the observed total value for both Ni^{2+} and Cu^{2+}ions.

TITRATION-II: Estimation of both Ni^{2+} & Cu^{2+} ions

Estimation of NI^{2+} & Cu^{2+}ions   **Indicator:** Muroxide & KNO_3

S. No.	Volume of NI^{2+}&Cu^{2+}ions (mL)	Burette Readings (ml)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

Titration III

The given ion solution is made up to 250 mL in a standard flask. 20mL of the solution is pipetted out into a conical flask. It is diluted with an equal volume of water. 5 mL of concentrated ammonia solution and 5 drops of the indicator solution are added. This is titrated against standard ETDA taken in the burette. Titrations are repeated till concordant results are obtained.

From the titre values strength of copper ion solution and the amount of copper in the whole of the given solution is calculated.

TITRATION-III: Estimation of Ni^{2+} ions only (Masking Method)

Estimation of Ni^{2+} ions   **Indicator:** Xylenol Orange + KNO_3

S. No.	Volume of Ni^{2+}ions (mL)	Burette Readings (mL)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

Calculation

Volume of EDTA required for Ni^{2+} ions only (x)   = (1 + 2) -3 =

Where

1 → Volume of EDTA added in titration –III for back titration
        = 20 mL

2 →Volume of EDTA required in titration – III for standardization of Ni^{2+} ions=

(Titration III burette Reading)

$3 \rightarrow$ Volume of EDTA required for titration – I for standardisation of ZnO =

$$X = (1 + 2) - 3 =$$

Volume of EDTA required for Cu^{2+} ions $(Y) = 4 – X =$

$4 \rightarrow$ Volume of EDTA required in titration –II for estimation of both Ni^{2+} & Cu^{2+} ions

$$Y=$$

STRENGTH OF NICKEL (II) IONS:

Volume of EDTA for Ni^{2+} (X) $V_1=$

Normality of EDTA $N_1 =$

Volume of Ni^{2+} ions $V_2 =$

Normality of Ni^{2+} ions $N_2 = \dfrac{V_1 \times N_1}{20mL} =$

The amount of Ni^{2+} ions present in the whole of the given solution =

$$= \dfrac{\text{Strength of the Ni2+ solution (N2) X Equivalent weitght of Ni2+ ion X 250}}{1000} =$$

$$\dfrac{\text{(N2) X 58.69 X 250}}{1000} =$$

STRENGTH OF COPPER (II) IONS:

Volume of EDTA for Cu^{2+} (Y) $V_1 =$

Normality of EDTA $N_1 =$

Volume of Cu^{2+} ions $V_2 = 20$ mL

Normality of Cu^{2+} ions $N_2 = \dfrac{V_1 \times N_1}{20ml} =$

The amount of Cu^{2+} ions present in the whole of the given solution =

$$= \dfrac{\text{Strength of the Cu2+ solution (N2) X Equivalent weitght of Cu2+ ion X 250}}{1000} =$$

$$\dfrac{\text{(N2) X 63.54 X 250}}{1000} =$$

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Amount Calculation:

The amount of Cu^{2+} ions present in the given
solution (in 250 mL)   =

The amount of Ni^{2+} ions present in the given
solution (in 250mL)   =

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mixture of cations-3

Result:

1. The amount of Cu^{2+} ions present in whole of the given
   solution =

2. The amount of Ni^{2+} ions present in whole of the given
   solution =

Complexometric
estimation of binary
mixture of cations-4

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Unit 10: Complexometric estimation of binary mixture of cations -4
Estimation of Fe^{3+}–Ni^{2+} mixtures using EDTA as a complexing agent by adopting anyone of the techniques, like precipitation, pH variation, masking and demasking.

Aim:

To estimate the individual amount of ferric and nickel ions present in whole of the given solution.

Principle:

A known excess of EDTA solution was added to the known volume of given solution. The unreacted excess EDTA was titrated against std. lead nitrate solution using xylenol orange indicator. Now the ferric ions were masked by converting it into ferric hydroxide then filtered through whatmann filter paper. The washings contains only Ni^{2+} ions. Then, known excess of EDTA solution was added to the washings. It was titrated against std. $Pb(NO_3)_2$ solution. This gives the titre value for Ni^{2+} ions only. By subtract the Ni^{2+} ion value from total value; we can get Fe^{3+} ions value.

Procedure: Stage 1

Standardisation of EDTA using std. $Pb(NO_3)_2$ solution:

About 0.33 g of ZnO was accurately weighed using electronic balance and dissolved in 2N HNO_3, made up in a 100 mL SMF. 20mL of this solution was pipetted out into a clean conical flask. The solution was diluted with 25mL of double distilled water. About 2mL of the buffer solution pH=10 and 2 drops of Eriochrome black –T indicator were added. The end point was noted when the colour changed from wine red to blue colour. The titrations were repeated for concordant titre values.

Calculation

Preparation of Std .Lead Nitrate solution

Weight of Lead Nitrate   = 0.33 g

Strength of Lead Nitrate $= \dfrac{1000 \times 0.331}{100 \times 331.21} = 0.01\ N$

Titration-I: Standardization of EDTA using std. Lead Nitrate solution

Indicator: xylenol orange + KNO_3 mixture

Complexometric
estimation of binary
mixture of cations-4

S. No.	Volume of Lead Nitrate (mL)	Burette Readings (mL)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of Lead Nitrate $\quad\quad\quad V_1 = 20$ mL

Normality of Lead Nitrate $\quad\quad\quad N_1 = 0.01$ N

Volume of EDTA $\quad\quad\quad\quad\quad V_2 =$

Normality of EDTA $\quad\quad\quad\quad N_2 = ?$

$$V_1N_1 = V_2N_2$$

Strength of EDTA $\quad\quad\quad N_2 = \dfrac{V1 \times N1}{V2} = \dfrac{20 \times 0.01}{V2} =$

Titration-II

Estimation of both (Fe^{3+} & Ni^{2+}) ions:

The given solution was made up into 100mL SMF. A known volume, say, 20ml of this made up solution was pipetted up in to a conical flask. About 40 ml (known excess) of std. EDTA was added to the beaker. Solid hexamine was added to maintain pH between 5 to 6. Five drops of xylenol orange indicator was added. When a yellow colour solution was obtained, the solution was titrated against std. lead nitrate solution. At the end point, the colour changed from yellow to red violet. From the titre value, the total amount of ferric and nickel ions present in the solution was calculated.

TITRATION-II: Estimation of both Fe^{3+} & Ni^{2+} ions

Estimation of Fe^{3+} & Ni^{2+} **ions** **Indicator:** Xylenol Orange + KNO_3

S. No.	Volume of Fe^{3+} & Ni^{2+} ions (mL)	Burette Readings (mL)		Volume of Lead nitrate(mL)
		Initial	Final	
1	20	0		
2	20	0		

NOTES

Titration-III

Estimation of Ni^{2+}ions (Precipitation Method):

A second aliquot of 20mL of mixture was pipetted out into a conical flask. The solution was warmed to 40ºC and about 1g of NH_4Cl solid was added to the solution. Then NH_4OH solution was added until the excess of ammonia was present. When ferric ion was precipitated as ferric hydroxide, the precipitate was digested over a water bath. It was filtered through whatmann filter paper No.41, washed with cold water and the washings were collected in a 400mL beaker. About 20ml of std. EDTA was added to the beaker. Solid hexamine was added to maintain the pH between 5 and 6. Five drops of xylenol orange indicator was added. The unreacted excess EDTA solution was titrated against std. lead nitrate solution. At the end point, the colour changed from yellow to red violet. From the titre value, the amount of Nickel ions present in the solution was calculated. The difference between the total and this value gives the amount of ferric ions present in the given solution.

TITRATION-III: Estimation of Ni^{2+} ions only (Masking Method)

Estimation of Ni^{2+} ions   **Indicator:** Xylenol Orange + KNO_3

S. No.	Volume of Ni^{2+} (mL)	Burette Readings (mL)		Volume of Lead nitrate (mL)
		Initial	Final	
1	20	0		
2	20	0		

CALCULATION

Normality of EDTA $N_1 =$

Normalityof $Pb(NO_3)_2$ $N_2 = 0.01\ N$

Volume of EDTA consumed for total ions **X** = 40 - $\dfrac{\text{Strength of Lead nitrate x volume of lead nitrate}}{\text{Strength of EDTA}}$

Volume of EDTA for both ions   **X** =

Volume of EDTA for Ni^{2+}only **Y**= 20

$-\ \dfrac{\text{Strength of Lead nitrate x volume of lead nitrate}}{\text{Strength of EDTA}}$

Volume of EDTA for Ni^{2+}only (**y**) =

52

Volume of EDTA for Fe^{3+}ion only = **X − Y** = _____

_____

Normality of Ni^{2+}ion $= \dfrac{Y \; x \; \text{Strength of Lead nitrate}}{20} =$

Normality of Fe^{3+}ion $= \dfrac{(X-Y) \; x \; \text{Strength of Lead nitrate}}{20} =$

The amount of Ni^{2+}ions present in the whole of the given

solution= $\dfrac{\text{Strength of the Ni2+solution (N2) X Equivalent weitght of Ni2+ ion X 250}}{1000} =$

$\dfrac{\text{(N2) X 58.69 X 250}}{1000} =$

The amount of Fe^{3+}ion present in the given solution =

$\dfrac{\text{Strength of the Ni2 + solution (N2) X Equivalent weitght of Ni2 + ion X 250}}{1000}$

$= \dfrac{\text{(N2) X 55.84 X 250}}{1000} =$

Result:

1. The amount of Fe^{3+} ions present in the whole of the given solution =

2. The amount of Ni^{2+} ions present in the whole of the given solution =

Complexometric
estimation of binary
mixture of cations-5

NOTES

Block-4
Unit 11: Complexometric estimation of binary mixture of cations -5

Estimation of Fe^{3+} – Pb^{2+} mixtures using EDTA as a complexing agent by adopting anyone of the techniques, like precipitation, pH variation, masking and demasking.

Aim:
    To estimate the individual amount of ferric and lead ions present in whole of the given solution.

Principle:
    A known excess of EDTA solution was added to the known volume of given solution. The unreacted excess EDTA was titrated against std. lead nitrate solution using xylenol orange indicator. Now the ferric ions were masked by converting it into ferric hydroxide then filtered through whatmann filter paper. The washings contains only Pb^{2+} ions. Then, known excess of EDTA solution was added to the washings. It was titrated against std. $Pb(NO_3)_2$ solution. This gives the titre value for Pb^{2+} ions only. By subtract the Ni^{2+} ion value from total value; we can get Fe^{3+} ions value.
    After the estimation of iron, the pH of the solution is suitably raised to 5 to 6 units and then titrate the Lead.

Procedure:
Stage 1
Standardisation of EDTA using std. $Pb(NO_3)_2$ solution:
    About 0.33 g of ZnO was accurately weighed using electronic balance and dissolved in 2N HNO_3, made up in to 100 mL SMF. 20mL of this solution was pipetted out into a clean conical flask. The solution was diluted with 25mL of double distilled water. About 2mL of the buffer solution P^H=10 and 2 drops of Eriochrome black –T indicator were added. The end point was noted when the colour changed from wine red to blue colour. The titrations were repeated for concordant titre values.

Calculation

Preparation of Std.Lead Nitrate solution

Complexometric
estimation of binary
mixture of cations-5

Weight of Lead Nitrate   = 0.33 g

Strength of Lead Nitrate $= \dfrac{1000 \times 0.331}{100 \times 331.21} = 0.01$ N

Titration-I: Standardization of EDTA using std. Lead Nitrate solution

Indicator: xylenol orange + KNO_3 mixture

S. No.	Volume of Lead Nitrate (mL)	Burette Readings (mL)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of Lead Nitrate V_1 = 20 mL
Normality of Lead Nitrate N_1 = 0.01 N
Volume of EDTA V_2 =
Normality of EDTA N_2 = ?

$$V_1 N_1 = V_2 N_2$$

Strength of EDTA $N_2 = \dfrac{V_1 \times N_1}{V_2} = \dfrac{20 \times 0.01}{V_2} =$

Titration-II

Estimation of both (Fe^{3+} & Pb^{2+}) ions:

The given solution was made up into 100mL SMF. A known volume, say, 20mL of this made up solution was pipetted up in to a conical flask. About 40 mL (known excess) of std. EDTA was added to the beaker. Solid hexamine was added to maintain pH between 5 to 6. Five drops of xylenol orange indicator was added. When a yellow colour solution was obtained, the solution was titrated against std. lead nitrate solution. At the end point, the colour changed from yellow to red violet. From the titre value, the total amount of ferric and lead ions present in the solution was calculated.

Complexometric
estimation of binary
mixture of cations-5

NOTES

TITRATION-II: Estimation of both Fe^{3+} & Pb^{2+} ions

Indicator: : Xylenol Orange + KNO_3

S. No.	Volume of Fe^{2+}&Pb^{2+} ions (mL)	Burette Readings (mL)		Volume of Lead nitrate (mL)
		Initial	Final	
1	20	0		
2	20	0		

Titration-II
Estimation of given solution
   The given solution is made up to 100mL in a 100mL SMF and the solution was shaken well for uniform concentration. Exactly 20mL of the solution was pipetted out into the conical flask. About 5mL of dil.HNO_3 was added to keep the pH of the solution in the range of 1-2 followed by 50 mg xylenol orange + KNO_3 mixture. The solution was titrated against standardized EDTA taken in the burette. The end point was colour changed from red–purple to yellow.
   Add hexamine solution (10 % w/v) until the colour becomes red-purple, add 1-2 mLmore. The titration was continued with the same EDTA solution until the colour changed from red to yellow. This gives the titre value for lead ion titration was repeated for concordant titre value.

Estimation of Pb^{2+} ion
    Volume of EDTA for Pb^{2+} $V_1 =$
    Normality of EDTA $N_1 =$
    Volume of Pb^{2+} ion $V_2 = 20$ mL
    Normality of Pb^{2+} ion $N_2 =$
    Normality of Pb^{2+} ion M_2 $= \dfrac{V1 \ X \ M1}{20ml} =$

The amount of Pb^{2+} ion (in 100mL) =

  =

$$\frac{\text{Strength of the given Pb2+ ion solution (M2) X Equivalent weitght of lead ion X 100}}{1000} =$$

The amount of lead(II) ions present in whole of the given solution =

Result:

1. The amount of iron ions present in whole of the given solution =
2. The amount of lead (II) ions present in whole of the given solution
   =

56

Complexometric
estimation of binary
mixture of cations-6

Unit 12: Complexometric estimation of binary mixture of cations -6
Estimation of Co²⁺-Cu²⁺ mixtures using EDTA as a complexing agent by adopting anyone of the techniques, like precipitation, pH variation, masking and demasking.

Aim

To estimate the amount of copper and cobalt ions present in the whole of the given solution.

Principle:

The copper and cobalt ions are estimated first with Murexide indicator. Then the copper(II) ions are masked selectively by adding thiourea in acidic medium, boiled and then cooled. Now the copper(II) ions are reduced to +1 state. Hence the EDTA cannot complexed with copper(I) cations. Here we get the value for cobalt ions only. On subtracting total value from cobalt value, we can get the amount of copper present in the given solution.

Procedure:

Titration-I

Standardization of EDTA using Std Lead Nitrate solution:

About 0.33 g of analar lead nitrate crystals was accurately weighed in an electronic balance and transferred it in to 250mL SMF and made up to the mark. About 20ml of this solution was pipetted out in to the clean conical flask and diluted with 25mL of water. Then 50mg of xylenol orange + KNO₃ mixture was added. Then powdered hexamine was added until the solution colour changed into intense red. It was titrated against EDTA taken in the burette. The end point was noted when the colour changed from pink to yellow. The titration was repeated to get concordant titre values.

Calculation

Preparation of Std .Lead Nitrate solution

Weight of Lead Nitrate	$= 0.33$ g
Strength of Lead Nitrate	$= \dfrac{1000 \times 0.331}{100 \times 331.21} = 0.01$ N

Titration-I: Standardization of EDTA using std. Lead Nitrate solution
Indicator: xylenol orange + KNO$_3$ mixture

S. No.	Volume of Lead Nitrate (mL)	Burette Readings (mL)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of Lead Nitrate $\quad\quad\quad$ V$_1$ = 20 mL

Normality of Lead Nitrate $\quad\quad\quad$ N$_1$ = 0.01 N

Volume of EDTA $\quad\quad\quad\quad\quad\quad\quad$ V$_2$ =

Normality of EDTA $\quad\quad\quad\quad\quad\quad$ N$_2$ = ?

$$V_1 N_1 = V_2 N_2$$

Strength of EDTA $\quad\quad\quad\quad\quad$ N$_2$ = $\dfrac{V1 \times N1}{V2} = \dfrac{20 \times 0.01}{V2} =$

Titration-II

Estimation of both (copper & cobalt) cations:

$\quad\quad\quad$ The given solution was made up to zero mark in a 250 mL SMF. Exactly 20mLof this made up solution was pipetted out in to a clean conical flask. The solution was diluted with 20mL of water. About 50 mg of muroxide/KNO$_3$ indicator mixture was added. Titration was carried out against standardized EDTA solution taken in the burette till the colour of the solution becomes pink. To this 4mL of pH=10 buffer solution was added. The solution turns yellow colour. Now the titration was continued till the end point reached. If the buffer solution was added before the commencement of the titration, turbidity appears which interferes with the titration. Hence the titration was carried out against EDTA solution without adding the buffer solution. After the addition of few mL of EDTA solution, the colour changed from yellow to pink. Now we add the buffer. The pink colour once again changed to yellow. This indicates the reaction was not completed. It further requires EDTA. The end point is the colour changed from yellow to pink. The titre value gives the volume of EDTA corresponding to the total amount of copper (II) and cobalt (II) ions present in the solution.

TITRATION-II: Estimation of both Cu^{2+} & Co^{2+} ions
Estimation of Cu^{2+} & Co^{2+} ions
Indicator: Muroxide& KNO_3

S. No.	Volume of Cu^{2+}& Co^{2+} ions (mL)	Burette Readings (mL)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

Titration-III
Estimation of cobalt (II) ions only [Masking Method]:

A second aliquot of 20mL of the made up solution was pipetted out into a clean conical flask. The solution was diluted with 25mL of double distilled water. About 5 drops of conc. HCl were added to make the solution acidic. The copper(II) ions were reduced to copper(I) ions by boiling the solution with 1 g thiourea. The solution was cooled. Then 20mL of EDTA solution was pipetted out into the flask. Cobalt(II)ions alone undergo complexation whereas copper(I) ions does not. The uncompleted EDTA was determined by adding exactly 20mL of lead nitrate solution. Then 50mg of xylenol orange+KNO_3 mixture and sufficient amount of hexamine were added until the solution becomes pink colour. The uncomplexed excess lead ions were back titrated against standardized EDTA solution. At the end point, the colour changed from pink to yellow colour. From the titre value, the volume of EDTA solution required to complex the cobalt(II)ions can be calculated. The difference between total and this value gives the volume of EDTA solution required to complex the copper(II) ions present in the given solution.

TITRATION-III: Estimation of Co^{2+} ions only (Masking Method)

Estimation of Co^{2+} ions   **Indicator:** Xylenol Orange + KNO_3

S. No.	Volume of Co^{2+}(mL)	Burette Readings (mL)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

Calculation

Volume of EDTA required for Co^{2+} ions only (x)   = (1 + 2) - 3
Where

1 → Volume of EDTA added in titration –III for back titration = 20 mL

2 → Volume of EDTA required in titration – III for standardization of Co^{2+} ions =

(Titration III burette Reading)

3 → Volume of EDTA required for titration – I for standardisation of $Pb(NO_3)_2$=

$$X =$$

Volume of EDTA required for Cu^{2+} ions   (Y) = 4 – X =

4 → Volume of EDTA required in titration –II for estimation of both Cu^{2+} &Co^{2+}ions =

$$Y =$$

ESTIMATION OF COBALT(II) IONS

Calculation

Volume of EDTA for Co^{2+}ions (X) $V_1=$

Normality of EDTA $N_1 =$

Volume of Co^{2+}ions $V_2 = 20$ mL

Normality of Co^{2+}ions $N_2 = \dfrac{V_1 \times N_1}{20mL}=$

The amount of Co^{2+} ion present in the whole of the given solution =

$$=$$

$$\dfrac{\text{Strength of the Co2+solution (N2) X Equivalent weitght of Co2+ ion X 250}}{1000} =$$

$$\dfrac{(N2)\ X58.93\ X\ 250}{1000} =$$

ESTIMATION OF COPPER(II) IONS

Volume of EDTA for Cu^{2+}(Y) $V_1=$

Normality of EDTA $N_1 =$

60

Volume of Cu^{2+} ions $\qquad V_2 = 20$ mL

Normality of Cu^{2+} ion $\qquad N_2 = \dfrac{V1 \times N1}{20mL} =$

The amount of Cu^{2+} ion present in the whole of the given solution =

$= $

$\dfrac{\text{Strength of the Cu2+solution (N2) X Equivalent weitght of Cu2+ ion X 250}}{1000} =$

$\dfrac{(N2) \times 63.54 \times 250}{1000} =$

Results:

1. The amount of Cu^{2+} ions present in whole of the given solution =
2. The amount of Co^{2+} ions present in whole of the given solution =

Complexometric
estimation of binary
mixture of cations-7

NOTES

Unit 13: Complexometric estimation of binary mixture of cations -7
Estimation of Zn^{2+}–Ca^{2+} mixtures using EDTA as a complexing agent by adopting anyone of the techniques, like precipitation, pH variation, masking and demasking.

Aim

    To estimate the individual amount of Zn^{2+} and Pb^{2+} ions present in whole of the given solution.

Procedure

Titration-I

Standardisation of EDTA using std. ZnO

    About 0.10 g of ZnO was accurately weighed using electronic balance and dissolved in 2N HNO_3, made up in 100mL SMF. 20mL of this made up solution was pipetted out into a clean conical flask. The solution was diluted with 25mL of water. About 2mL of pH=10 buffer and two drops of Eriochrome black-T indicator were added. The end point was noted when the colour changed from wine red to blue colour. Titrations were repeated for concordant titre values.

STAGE-I

Preparation of Std. Zinc Oxide solution

Weight of Zinc Oxide   = 0.1 g

Normality of Zinc Oxide $= \frac{0.10 \times 1000}{100 \times 81.4} = 0.0122$ N

TITRATION-I

Standardisation of EDTA using std. ZnO
Indicator: Eriochrome black-T

S. No.	Volume of ZnO (mL)	Burette Readings (mL)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of Zinc Oxide	$V_1 = 20$ mL
Normality of Zinc Oxide	$N_1 = 0.012$ N
Volume of EDTA	$V_2 =$
Normality of EDTA	$N_2 = ?$

$$V_1N_1 = V_2N_2$$

Strength of EDTA $\qquad\qquad N_2 = \dfrac{V1 \times N1}{V2} = \dfrac{20 \times 0.012}{V2} =$

Titration-II

Estimation of both (Zinc & Calcium) ions

The given solution was made up with 250mL SMF. Then 20mL of this solution was pipetted out into a clean conical flask. It was diluted to 50mL, and then 5mL of Eriochrome black-T indicator was also added. Then the solution was titrated against standardized EDTA taken in the burette. The end point was noted at the colour changes from wine red to blue. This value is the observed total value for both Zn^{2+} and Ca^{2+} ions.

TITRATION-II: Estimation of both Zn^{2+} & Ca^{2+} ions

Estimation of both Zn^{2+} & Ca^{2+} ions **Indicator:** Eriochrome black-T

S. No.	Volume of Zn^{2+} & Ca^{2+} ions (mL)	Burette Readings (mL)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

TITRATION-III: Estimation of Ca^{2+} ions only (Masking Method)

Titration-III

Estimation of Ca^{2+} ions only [Masking Method]

Exactly 20mL of the given made up solution was pipetted out into another conical flask. About 50mg of sodium diethyl dithiocarbomate was added to the solution to mask Pb^{2+} ions. Then 20mL of std EDTA solution and 20mL of std. Zn^{2+} solution were added for back titration. Then 4mL of pH=10 buffer and two drops of EBT indicator were added. The excess of Zn^{2+} was titrated against standardized EDTA until the end point of colour change from wine red to blue. This is the titre value only for Ca^{2+} ions. The titration was repeated for concordance.

Pb^{2+}	+	HY^{3-}	$\xrightleftharpoons{pH = 10}$	PbY^{2-}	+	HY^{3-}	
analyte Colorless		excess known amount (EDTA) colorless		metal ion-EDTA complex (colorless)		unreacted EDTA (colorless	

HY^{3-}	+	HIn^{2-}	+	Zn^{2+}	$\xrightleftharpoons{pH = 10}$	ZnY^{2-}	+	ZnY^{2-}	+	H^+
unreacted EDTA (colorless)		Free indicator		titrant (colorless)		metal ion-EDTA complex (colorless)		metal ion-indicator complex (wine-red)		

63

Complexometric
estimation of binary
mixture of cations-7

NOTES

Estimation of Ca^{2+} ions   **Indicator:** Eriochrome black-T

S. No.	Volume of Ca^{2+}(mL)	Burette Readings (ml)		Volume of EDTA (mL)
		Initial	Final	
1	20	0		
2	20	0		

Volume of EDTA required for Ca^{2+} ions only (x)   = (1 + 2) -3
Where

1 → Volume of EDTA added in titration –III for back titration
        = 20 mL

2 →Volume of EDTA required for titration – III for Ca^{2+} ions only =
———

                                    (Titration III burette Reading)

3 →Volume of EDTA required for titration – I for standardisation of ZnO

                                    X =

ESTIMATION OF CALCIUM (II) IONS:

Volume of EDTA for Ca^{2+} $V_1=$

Normality of EDTA $N_1 =$

Volume of Ca^{2+} ions $V_2= 20$ mL

Normality of Ca^{2+} ion $N_2= \dfrac{V_1 \times N_1}{20ml}=$

The amount of Ca^{2+} ion present in the whole of the given solution =
    =
$\dfrac{\text{Strength of the Ca2+solution (N2) X Equivalent weitght of ca2+ ion X 250}}{1000}=$

$\dfrac{\text{(N2) X 40.07 X 250}}{1000}=$

    =

ESTIMATION OF ZINC(II) IONS:

Volume of EDTA required for Zn^{2+} ions (Y) = 4 - x =

Where 4 → titration II end point

Calculation

Volume of EDTA for Zn^{2+}	$V_1 =$
Normality of EDTA	$N_1 =$
Volume of Zn^{2+} ions	$V_2 = 20$ mL
Normality of Zn^{2+} ions	$N_2 = \dfrac{V_1 \times N_1}{20mL} =$

The amount of Zn^{2+} ion present in the whole of the given solution =

$$= \frac{\text{Strength of the Zn2+solution } (N_2) \times \text{Equivalent weitght of Zn2+ ion} \times 250}{1000} =$$

Results:
1. The amount of Ca^{2+} ions present in whole of the given solution =
2. The amount of Zn^{2+} ions present in whole of the given solution =

Complexometric estimation of binary mixture of cations-7

NOTES

Self-Instructional Material

Determination of
total, permanant and
temporary hardness
of water by
complexometry

NOTES

Unit 14: Determination of total, permanant and temporary hardness of water by complexometry

Water containing high amounts of dissolved minerals is called hard water. Hardness of water is generally due to the presence of bicarbonate, chloride and sulfate salts of calcium and magnesium ions. Presence of these cations in water significantly decreases the cleaning action of soaps. Water hardness is of two types, temporary and permanent. Temporary hardness is due to the presence of bicarbonate salts of calcium and magnesium. It can be removed by boiling. On the other hand, permanent hardness is due to the presence of chloride and sulfate salts of calcium and magnesium, which cannot be removed by boiling.
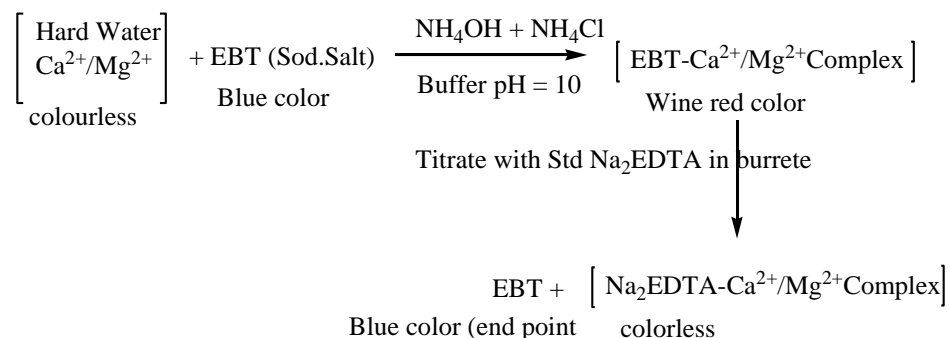
Chemicals and equipments required

Water samples, standard Na_2EDTA solution, standard hard water (SHW), ammonia buffer solution (pH 10 ± 1), Eriochrome black- T(EBT sod. salt) indicator, burette, pipette, conical flask etc.

Water hardness is, in general, expressed as the measure of total concentration (ppm) of calcium and magnesium ions expressed as calcium carbonate. It is determined by performing complexometric titration using a standard sodium salt of ethylenediaminetetraacetic acid (Na_2EDTA) solution. Eriochrome black T indicator, which is an azo dye is used as indicator to determine the endpoint of this complexometric titration.

Eriochrome black T forms a wine red coloured weak complex with calcium ions present in hard water. During the course of titration, Na_2EDTA solution is added to the hard water. Na_2EDTA abstracts all the calcium ions from wine red coloured complex. That means at end point of this titration calcium-indicator complex breaks down completely and all the calcium ions form chelate with Na_2EDTA and solution turns blue in colour (**Scheme 1**).

The blue colour is due to the presence of Eriochrome black T in ammonia buffer solution.

$$\begin{bmatrix} \text{Hard Water} \\ Ca^{2+}/Mg^{2+} \\ \text{colourless} \end{bmatrix} + \underset{\text{Blue color}}{\text{EBT (Sod.Salt)}} \xrightarrow[\text{Buffer pH} = 10]{NH_4OH + NH_4Cl} \underset{\text{Wine red color}}{\begin{bmatrix} \text{EBT-}Ca^{2+}/Mg^{2+}\text{Complex} \end{bmatrix}}$$

Titrate with Std Na_2EDTA in burrete

$$\underset{\text{Blue color (end point}}{\text{EBT} +} \underset{\text{colorless}}{\begin{bmatrix} Na_2EDTA\text{-}Ca^{2+}/Mg^{2+}\text{Complex} \end{bmatrix}}$$

(I) Preparation of Na₂EDTA Solution: 0.01N aqueous solution of Na$_2$EDTA is prepared by in distilled water and making the volume up to one liter (This solution can be standardized by titration against standard solution of magnesium sulfate).

(II) Preparation of ammonia buffer (pH = 10±1): Weighed 17 gm of NH$_4$Cl and dissolve in 142.5 ml of concentrated aqueous ammonia solution and subsequently dilute to 250 mL with distilled water.

(III) Preparation of standard hard water (SHW): Prepare 1000 ppm standard hard water as follow:-

Weigh 0.1g CaCO$_3$ and transfer it in 100 mL (1.0mg/L = 1.0ppm) volumetric flask add about half test tube of HCl to dissolve CaCO$_3$ and make up the volume by adding distilled water up to the mark of 100 mL. CaCO$_3$ is insoluble hence is first converted to water soluble CaCl$_2$ by treating it with HCl.

Procedure:

Rinse and fill the burette with 0.01N Na$_2$EDTA solution. Pipetted out 10 mL of SHW in aconical flask, add 2 mL of buffer solution add two-three drops of EBT indicator. Wine red colour is obtained. Titrate the reaction mixture with Na$_2$EDTA solution taken in burette till blue colour appears at the end point. Note the reading of burette and repeat the same process till three concordant readings are obtained (V1). Similarly follow the same process for unknown hard water. The volume of Na$_2$EDTA solution used corresponds total hardness (V2). Tabulate your results in observation table. For permanent hardness, take 250 mL of hard water in a 500mL beaker and boil till it reduces half. Filter the solution in 250mL flask and add distilled water to make the final volume of 250mL. Titrate 10 mL of this solution using buffer and EBT as indicator. The volume of Na$_2$EDTA solution used in this step corresponds permanent hardness (V3). Tabulate your results in observation table.

Observations:
(i) Reading with SHW

S. No.	Volume of standard hard water (mL)	Burette Readings (mL)		Volume of EDTA (mL) V1
		Initial	Final	
1	10	0		
2	10	0		

Reading with unknown hard water

S. No.	Volume of unknown hard water (mL)	Burette Readings (mL)		Volume of EDTA (mL) V2
		Initial	Final	
1	10	0		
2	10	0		

Reading after boiling the solution (Permanent hardness)

S. No.	Volume of boiled hard water (mL)	Burette Readings (mL)		Volume of EDTA (mL) V3
		Initial	Final	
1	10	0		
2	10	0		

Calculations:
The hardness of the water sample is calculated in parts of $CaCO_3$ per million of water (ppm).
(i) 1 mL of SHW = 1 mg $CaCO_3$

$V1$ mL Na_2EDTA = 10 mL SHW solution = 10 mg $CaCO_3$

1 mL Na_2EDTA = $10/V1$ mg $CaCO_3$

(ii) Total hardness
10 mL unknown hard water = V_2 mL Na_2EDTA solution = $V_2 \times 10/V_1$ mg $CaCO_3$

1mL unknown solution = $V_2/V_1 \times 10/10$ mg $CaCO_3$

1000 mL unknown solution = $V_2/V_1 \times 1000$ mg $CaCO_3$

Total hardness = $V_2/V_1 \times 1000$ mg $CaCO_3$

= $V_2/V_1 \times 1000$ ppm

(iii) Permanent hardness

10 mL boiled hard water = V_3 mL Na_2EDTA solution

Permanent hardness = $V_3/V_1 \times 1000$ ppm

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(iv) Temporary hardness

Total hardness – Permanent hardness

Results:

(i) Total hardness of given water sample is _____ ppm.

(ii) Permanent hardness of water sample is _____ppm

(iii) Temporary hardness of water sample is _____ppm

NOTES

Determination of
total, permanant and
temporary hardness
of water by
complexometry

Question

1. Explain why EDTA has the widest general applications in compleximetry.
2. Show by drawing the effect of apparent stability constant and of ph on EDTA titration curves.
3. Draw spatial structure of Ca-EDTA chelate.
4. Write about Chemical structure of a metallochromic indicator.

1. What Is Decinormal Solution?

The solution that contains 1/10th gram equivalent of solute in one liter of its solution is called decinormal solution.

2. What are the requisites for a substance to be a Primary Standard? Mention Its Examples.

The criteria for a solution to be primary standard solution are as follows:

1. It should be available in pure and dry state.
2. Its composition should not be changed on storage. I.e., It should not be toxic, volatile, hygroscopic and deliquescent.
3. It should be highly soluble in water without any change in its composition.
4. It should have higher molecular and equivalent weight.

Some of the examples of primary standard solution are:

Sodium carbonate (Na_2CO_3), Potassium dichromate ($K_2Cr_2O_7$), oxalic acid $(COOH)_2.2H_2O$, Mohr's salt etc.

3. What is titration?

The process of adding one solution from the burette to another in the titration flask in order to complete the chemical reaction involved, is known as titration

4. What is indicator?

Indicator is a chemical substance which changes colour at the end point.

5. What is end point?

The stage during titration at which the reaction is just complete is known as the end point of titration

6. What is secondary standard solution?

The standard solution whose concentration is measured with the help of primary standard solution is called secondary standard solution.

Example: naoh, hcl, h₂so₄ etc.

7. What are the differences between end point and equivalence point?

End point is the point which indicates the completion of reaction by changing its color. It is indicated by the indicator. While equivalence point is the theoretical point at which the equivalent amount of titrand and titrant are added together. It is a theoretical point.

8. What is indicator and write its types?

1. Self indicator
2. Internal indicator

3. External indicator

9. What is standard solution?

The solution of accurately known strength is called the standard solution and it contains known weight of the solute in a definite volume of the solution.

10. Will you read upper or lower meniscus of kmno4solution in a burette?

Upper meniscus in case colored solution.

11. Differentiate b/w equivalence & endpoint in titrations?

The point at which the reaction b/w titrant & titrate is just complete is called equivalence point or theoretical point.

The point at which a clear visual change is observed after the reaction b/w titranta and titrate is practically complete is end point.

Thus there exists a very small difference b/w the end point & equivalence point.

12. What is meant by the term 'concordant readings'?

The readings in volumetric analysis which differ by less than 0.05 ml eire known as concordant readings

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Determination of total, permanant and temporary hardness of water by complexometry

NOTES

Self-Instructional Material

Alagappa University
Directorate of Distance Education
Practical Examination for M. Sc., Chemistry

II Year – III Semester

34434 Inorganic Chemistry Practical

Time: 6 Hrs   **Marks: 75**

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Answer the following

A.	Estimate the given mixture of copper-nickel solution, copper by volumetrically – nickel by gravimetrically and report the amount of copper and nickel ions present in whole of the given solution.
B.	Estimate the given mixture of bismuth- lead solution complexometrically and report the amount present in whole of the given solution

Distribution of Marks

Distribution	Procedure	Results for Four ions & execution	Viva-voce	Record work	Total Marks
Marks	15	40	10	10	75