Some Selected Experiments in Inorganic Chemistry

By

Professor S. N. Dindi M.Sc., Ph. D.

Department of Chemistry

GITAM Institute of Science

G I T A M

(Deemed to be University, Estd. U/s 3 of the UGC Act, 1956)

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Visakhapatnam - Hyderabad - Bengaluru

General Instructions

1. Study theory behind the experiment before attending the Laboratory

2. Keep the work bench and sink (wash basin) neat and clean. Do not allow used filter papers, broken pieces of glass, used match sticks, etc., to lie on the work bench – throw them into the available dust bin nearby.

3. Keep the apparatus clean and arrange them properly.

4. Handle the chemicals and reagent bottles carefully.

5. Take the prescribed quantities of chemicals and reagents only.

6. Do not pour any excess reagent, taken by chance, back into the reagent bottle, as it is likely to contaminate the entire solution in the reagent bottle.

7. Close the reagent bottles with their lids and keep them in their proper places, after use.

8. Water is a precious commodity; do not waste it; close the water tap immediately after use.

9. It is said, 'Prevention is better than cure' - take care to prevent fire accidents in the Lab.

10. If any piece of apparatus is broken, promptly bring it to the notice of either Staff Member or Lab Assistant.

11. Make it a habit to record all observations in your Observation Note Book, as and when you carry out an experiment; writing observations on loose bits of paper is a bad habit.

12. Do not forget to bring your Laboratory Record while attending the lab.

13. Always wear shoes and laboratory apron while you are in the lab.

14. Wash chemical spills on your body, if any, immediately with plenty of tap water.

15. Before leaving the Laboratory, wash the apparatus clean, keep them in proper place and make your work bench tidy.

16. Remember that it is the practice to write the Lab Record in passive voice.

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III. Gravimetric Analysis

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Introduction

The objective of a chemical analysis is to detect and identify different constituents present and finally determine their relative amounts in a substance. The process of detection and identification is commonly known as **Qualitative Chemical Analysis** (*Qualitative Analysis*) while the determination of the amounts of the constituents as **Quantitative Chemical Analysis** (*Quantitative Analysis*). Depending upon the technique used for the determination of the amount, the quantitative chemical analysis can be broadly divided into **Gravimetric Analysis** and **Titrimetric** (***Volumetric***) **Analysis**; the name **Titrimetric Analysis** is preferred over *Volumetric Analysis* as the later, now a day, means determination of volume of a gas evolved in a chemical reaction.

Gravimetric analysis is the process of isolating and weighing an element or a definite compound of the element in as pure a form as possible. The element or compound is precipitated from the solution of a weighed portion of the substance being examined. On the other hand, titrimetric analysis essentially consists in determining the volume of a solution of accurately known concentration which is required to react quantitatively with a known volume of the solution of the substance being determined. The solution of accurately known **strength** (***concentration***) is called the **Standard solution**; it contains a definite number of gram equivalents or gram moles per liter of the solvent. The weight of the constituent aimed to be determined is then calculated from the volume of the standard solution consumed and known laws of chemical equivalence. In practice, a standard solution is prepared by dissolving a known weight of the **primary standard substance** in a known volume of water (solvent). In general, in order to serve as a primary standard, the substance has to satisfy the following requirements:

a) It must be easy to obtain, to purify, to dry (preferably at 110 – 120 ^{0}C), and to preserve in a pure state.

b) The substance should be unaltered in air during weighing; it should not be hygroscopic, efflorescent, oxidized by air, or affected otherwise.

c) It must be a high purity substance; impurities should not exceed 0.01 – 0.02 per cent.

d) It should have reasonably high equivalent weight so that the weighing errors are negligible.

e) It should be readily soluble in the solvent.

f) The reaction of the standard solution with the analyte solution should be stoichiometric and practically instantaneous.

In practice, an ideal primary standard substance which satisfies all the above criteria is difficult to obtain and a compromise among the above ideal requirements is usually necessary. Some of the commonly employed primary standard substances are: Na_2CO_3, KCl,

$K_2Cr_2O_7$, $Na_2C_2O_4$, $KBrO_3$, KIO_3, $(NH_4)_2$ $Ce(NO_3)_6$, and As_2O_3. Hydrated salts, as a rule, do not make good standards, because of the difficulty of efficient drying. However, hydrated salts which do not effloresce, such as oxalic acid $H_2C_2O_4$ $2H_2O$ and copper sulphate $CuSO_4$ $5H_2O$ are found to be satisfactory secondary standards. The solutions prepared from less stable compounds need to be standardized using a primary standard solution before use.

The **Standard Solution** (***Titrant***) is usually added form a burette. The process of adding the standard solution to the solution (***Titrand***/***Analyte***) taken in the conical flask (titration/reaction vessel) until the reaction is just complete is termed as **Titration.** The point at which the reaction is just complete is called **Equivalence Point** or **Theoretical** (or **Stoichiometric**) **End Point.** The completion of the reaction should be detectable by some change, unmistakable to the eye, produced by the standard solution itself (e.g., $KMnO_4$) or more usually by the addition of an auxiliary reagent, known as **Indicator**. After the reaction is practically complete, the indicator would give a clear visual change (colour change or formation of turbidity) in the solution being titrated (***titrand/analyte***). The point at which this occurs is called the **End Point** of the titration.

For the purpose of discussion, the titrimetric analysis can be divided into four main types:

1. Neutralisation reactions or **Acidimetry** and **Alkalimetry**. These include the titration of free bases or those formed by hydrolysis of salts of weak acids, with a standard acid (**Acidimetry**) as well as the titration of free acids, or those formed by the hydrolysis of salts of weak bases with a standard base (**Alklimetry**). In these reactions, hydrogen and hydroxide ions combine to form water.

$$H^+ + OH^- \longrightarrow H_2O$$

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

2. Oxidation – reduction or **Redox reactions**. These are the reactions involving change in oxidation number or transfer of electrons among the reacting substances. In these reactions, the substance which loses electrons is called a **Reducing agent** or **Reductant** while that which gains electrons an **Oxidising agent** or **Oxidant**; the overall reaction between the reductant and the oxidant is called **Redox reaction**.

$$2\,Fe^{III}Cl_3 + Sn^{II}Cl_2 \longrightarrow 2Fe^{II}Cl_2 + Sn^{IV}Cl_4$$

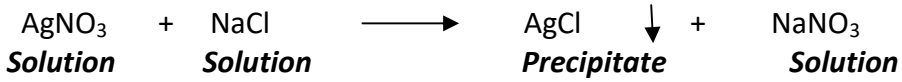
Oxidant ***Reductant***

3. Complex formation reactions. These depend upon the combination of ions or molecules, other than hydrogen and hydroxide ions, to form a soluble, slightly dissociated ion or compound.

$$CuSO_4 + 4KCN \longrightarrow K_2[Cu(CN)_4]\ (Complex) + K_2SO_4$$

$$Ag^+ + 2CN^- \longrightarrow [Ag(CN)_2]^-\ (Complex)$$

4. Precipitation reactions. These reactions involve precipitation of sparingly soluble compounds from solutions of the two reactants.



Usually, the strength of a solution is expressed either in **Molarity** or in **Normality**. A **molar solution** (**1M**) is one which contains one **gram molecular weight** (***gram mole***) of the reagent per liter of the solution. Similarly, a **normal solution** (**1N**) of a substance contains one gram equivalent weight of it per liter of the solution. Even though the gram molecular weight of a reagent does not vary, the gram equivalent weight varies with the type of the reaction; the same compound possesses different gram equivalent weights in different contexts.

In neutralization reactions, the gram equivalent weight of an acid is obtained by dividing the gram molecular weight of it by the number of replaceable hydrogen ions that it contains. For example, the gram equivalent weight of HCl is its gram molecular weight divided by **one** (36.45/1), while that for H_2SO_4 is its gram molecular weight divided by **two** (98/2 = 49). Similarly, the gram equivalent weight of a base is obtained by dividing its molecular weight by the number of replaceable hydroxide ions that it contains. For example, the gram equivalent of $Ba(OH)_2$ is its gram molecular weight divided by **two** as it contains two replaceable hydroxide ions.

With reference to redox reactions, the gram equivalent weight of an oxidant is obtained by dividing its gram molecular weight by the number of electrons that it gains while that of a reductant by dividing its gram molecular weight by the number of electrons it loses in the reaction. For example, thallous chloride (TlCl) is a reductant and loses two electrons in the process of oxidation and hence its gram equivalent weight is obtained by dividing its gram molecular weight by **two** (239.83/2 = 119.92). The case of $KMnO_4$ is very interesting. As an oxidant, it may gain one, three, four or five electrons depending upon the condition of the reaction medium and accordingly its gram equivalent varies as 158/1, 158/3, 158/4 and 158/5 respectively.

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Description of Apparatus

While carrying out experiments in Inorganic Chemistry Lab, you are going to use the following glass apparatus.

Burette: The commonly used laboratory burette (Fig. 1) is a long glass tube of uniform bore throughout its length. It has a holding capacity of 50 mL and is graduated up to $1/10^{th}$ of a milliliter, from top to bottom. At its lower end, a stopcock with nozzle is fixed to facilitate control of flow of a solution at the desired rate. You have to note the following points whenever you use a burette.

a) The burette should always be kept absolutely clean. For this purpose, it should be cleaned with chromic acid, thoroughly washed with tap water and then rinsed with distilled water.

b) Before starting the titration, it should be rinsed with the standard solution, filled with the same solution up to the zero mark, taking care to avoid air gaps in the nozzle and air bubbles in the stem and then fixed to burette stand, vertically (Fig. 2).

c) While noting down the burette readings, the lower meniscus of the solution in the burette has to be kept at the eye level to avoid parallax error; with dark coloured solutions like potassium permanganate, the lower meniscus may not be clearly visible and in such instances the upper meniscus is the choice.

Volumetric or **transfer** or **single mark Pipette**: It is a long narrow tube having cylindrical bulb in the middle, tapering into a fine nozzle at its lower end and an etched circular mark a little above the bulb on the upper truncated end. The volume of liquid delivered on starting from the etched mark to the tip of the nozzle is printed on the bulb of the pipette, in milliliters. As it is useful in transferring the same volume of a liquid always, it is called single mark pipette (Fig. 3). *Caution*: Do not blow off the little amount of liquid that remains at the tip of the nozzle, after transfer.

Volumetric Flask: A volumetric flask is a flat-bottomed, pear shaped vessel with a long narrow neck fitted with leak proof lid at the top (Fig. 5B). A thin line etched around the neck indicates the volume that it holds at a certain definite temperature (both the capacity and temperature are clearly marked on the flask). It is used in preparation of standard solutions and dilution of a sample to a definite volume. Flasks with capacities ranging from 5 mL to 2 Liters are in use.

Graduated pipette: It is similar to a burette with a nozzle, but lacks a stopcock (Fig. 4). The regulation of flow of a liquid can be manipulated with forefinger kept at its top end. Just like a burette, it is useful in transferring variable volumes. There are pipettes with different total capacities starting from 1 mL and above.

Measuring Jar or Measuring Cylinder: This is a cylindrical jar provided with a sturdy base. It is graduated from bottom to top (Fig. 6). Usually, the diameter of the cylinder is relatively

large and hence is useful for transfer of approximate volumes of reagents only. Jars with holding capacity ranging from 10 mL to 2 Liters are available.

Beaker: Beaker is a flat bottomed wide cylinder with or without a spout at the top (rim) (Fig. 7). Beakers with capacities ranging from 5 mL to 2 Liter are in use. However, 250 mL and 400 mL beakers are more common in student laboratories. They are useful in preparation and handling of reagents, titrimetric and gravimetric analysis.

Conical flask or Erlenmeyer's Flask: It is a cone shaped flask with a flat bottom, mostly used as a reaction vessel in carrying out a titration (Fig. 5A). Even though flasks with capacities ranging from 10 mL to 1 Liter are available, 250 mL and 500 mL flasks are more commonly used.

Wash Bottle: A wash bottle is a flat bottomed flask designed to deliver a fine jet of distilled water or other liquid. This is used as a small size reservoir for storing and transfer of distilled water. It finds wide application in cleaning laboratory ware also. Both glass and squeeze type polythene bottles (Fig. 8) are known but, the latter type, now a day, finds wider application. They are available from 100 mL to 1 Liter capacities.

Glazed Tile: It is a ceramic plate glazed white on one side. It helps to perceive the colour change at the end point of a titration by providing a glossy white back ground.

Pictures of Some Apparatus and Equipment Used in the Lab

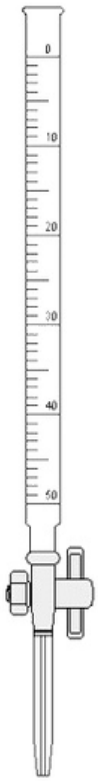

Fig. 1: Burette

Fig. 2: Burette and Clamp fixed to Stand

Fig. 3: Volumetric Pipettes

Fig. 4: Graduated Pipette

A B C

Fig. 5: Different types of Flasks

A - Conical Flask; B - Volumetric Flask; C – Round bottomed flask.

Fig. 6: Measuring Cylinders

Fig. 7: Beaker

Fig. 8: Polythene Wash Bottles

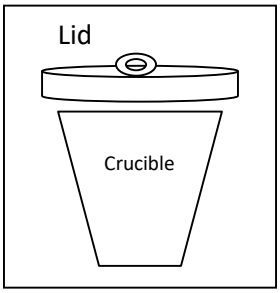

Fig. 9: Crucible with lid Glass

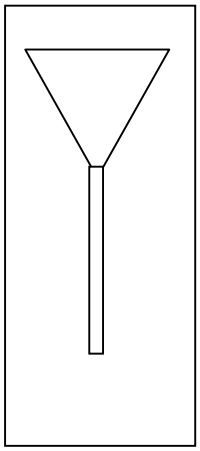

Fig. 10: Funnel

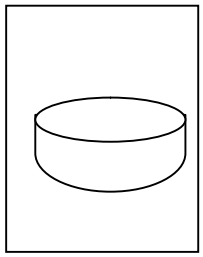

Fig. 11: Evapourating dish

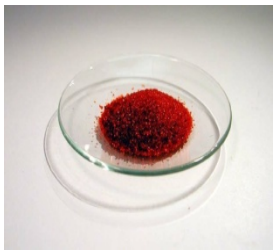

Fig.12: Watch

I. SYNTHESIS OF INORGANIC COMPOUNDS

1. Preparation of ammonium ferrous sulphate hexahydrate $(NH_4)_2SO_4\ FeSO_4\ 6H_2O$

PROCEDURE

Warm 50 mL of 2 N sulphuric acid with an excess of iron nails taken in a conical flask. When the reaction between iron nails and sulphuric acid subsides, filter the mass into a clean evaporating dish. Add to the filtrate 5 mL of 2 N sulphuric acid followed by a solution containing 8.3 g of ammonium sulphate in 25 mL of water. Mix it well, evaporate the resultant solution to the point of crystallization by heating and allow the solution to cool to room temperature. Separate the crystals formed from the mother liquor and recrystallise the substance using minimum amount of water and 5 mL of 2 N sulphuric acid. Filter the crystals, dry and report the yield.

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2 \uparrow$$

$$\underset{\textit{Salt}}{FeSO_4} + \underset{\textit{Salt}}{(NH_4)_2SO_4} + 6H_2O \longrightarrow \underset{\textit{Double salt}}{(NH_4)_2Fe\,(SO_4)_2\,6H_2O}$$

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2. Preparation of tetraamminecopper(II) sulphate monohydrate $[Cu(NH_3)_4]\ SO_4\ H_2O$

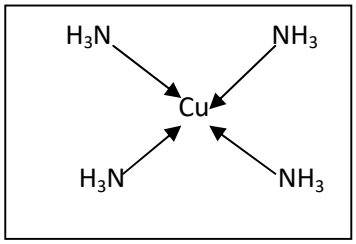
PROCEDURE

Dissolve 1 g of copper sulphate pentahydrate, $CuSO_4\ 5H_2O$ in the minimum quantity of water in a 100 mL beaker and add with stirring 10 mL of concentrated ammonia to it. The first formed bluish white precipitate dissolves, the solution assumes dark blue colour and strongly smells ammonia. Carefully add to the solution 10 mL of rectified spirit down the sides of the beaker such that a separate alcohol layer forms over the aqueous layer. Cover the beaker with a watch glass and allow the complex to crystallize. After the crystallization is completed, filter the crystalline material, dry, weigh and report the yield as early as possible.

$$\underset{\textit{Blue}}{Cu\,SO_4} + 2NH_4\,OH \longrightarrow \underset{\textit{Bluish white ppt.}}{Cu\,(OH)_2} + 5H_2O + (NH_4)_2\,SO_4$$

$$\downarrow \text{Excess ammonia}$$

$$\underset{\textit{Violet blue complex}}{[Cu\,(NH_3)_4]\,SO_4\,H_2O}$$



SO_4 H_2O

Fig. Structure of $[Cu(NH_3)_4]$ SO_4 H_2O

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3. Preparation of tris(thiourea)copper(I) sulphate dihydrate $[Cu(tu)_3]_2$ SO_4 $2H_2O$

Solutions

1. Thiourea solution: Dissolve 6.0 g of thiourea in 40 mL of hot distilled water in a 100 mL beaker and cool the solution to room temperature.

2. Copper sulphate solution: Dissolve 4.0 g of copper sulphate pentahydrate in 20 ml of distilled water in a 100 mL beaker.

PROCEDURE

Take 25 mL of the cold thiourea solution in a 100 mL conical flask and add to it the prepared copper sulphate solution in small portions; thorough mixing of the thiourea solution while the copper sulphate solution is being added is essential. Cool the conical flask with its contents in a cold water bath until the separated yellowish oil settles at the bottom of the flask. Decant and reject the upper aqueous layer. While vigorously shaking the oily mass in the conical flask, add to it 13 mL of thiourea solution and continue the vigorous shaking until crystallization of the complex is complete. Filter and wash the crystals with a small volume of distilled water. Finally dry the crystals and report the yield.

$$2\ CuSO_4 \xrightarrow{CS(NH_2)_2} Cu_2\{CS(NH_2)_2\}_2\ SO_4 \xrightarrow{CS(NH_2)_2} Cu\{CS(NH_2)_2\}_3]_2\ SO_4 .2H_2O$$

Blue coloured solution ***Yellow coloured oily liquid*** ***Pale yellow crystalline solid***

The crystal structure of the compound is ionic consisting of infinite chain of $[Cu\{CS(NH_2)_2\}_3]^+$ cationic units and SO_4^{2-} anions. The chain consists of tetrahedral units of $[Cu\{CS(NH_2)_2\}_3]$ interlinked through bridging $CS(NH_2)_2$ ligands at the corners the tetrahedra. For the sake of clarity, the complex cation is often represented as $[Cu(tu)_3]_2^{2+}$ where tu stands for **t**hio**u**rea as ligand.

Precautions: 1. Separate the settled yellowish oily product from its mother liquor as soon as possible.

2. Do not start the procedure with warm solution of thiourea; always start with a cold and clear solution of thiourea..

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4.Preparation of potassium tris(oxalato)aluminate(III) trihydrate $K_3[Al(C_2O_4)_3]\ 3H_2O$

Solutions

1. Aluminium sulphate solution: Dissolve 2.0 g of aluminium sulphate in 40 mL of water in a 250 mL beaker.

2. Ammonium hydroxide solution (1 : 1): Mix 10 mL of concentrated ammonia with 10 mL of water in a 100 ml conical flask and cover the conical flask with a watch glass.

3. Mixed solution of oxalic acid and potassium oxalate: Dissolve 1.2 g of oxalic acid and 1.5 g of potassium oxalate in 100 mL of water in a 250 mL beaker.

PROCEDURE

To the aluminium sulphate solution contained in the beaker, slowly add with stirring 20 mL of 1:1 ammonium hydroxide solution. Filter off the aluminium hydroxide precipitate from the mother liquor and wash the precipitate twice with small quantities of water. Transfer the aluminium hydroxide precipitate into the beaker containing the mixed solution of oxalic acid and potassium oxalate and heat the contents of the beaker to dissolve the precipitate. Filter off any undissolved material. Evaporate the filtrate; stop evaporation when a slight encrustation is noticed to form at the top of the solution and allow crystallization of the complex to take place by slow cooling. Filter the crystals, dry them and report your yield.

$$Al_2(SO_4)_3 + 2\,H_2C_2O_4 + 4\,K_2C_2O_4 \longrightarrow 2K_3[Al(C_2O_4)_3 + K_2SO_4 + 2H_2SO_4$$

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5. Preparation of potassium tris(oxalato)ferrate(III) trihydrate $K_3[Fe(C_2O_4)_3]\ 3H_2O$

Solutions

1. Ammonium ferrous sulphate solution: Dissolve 2 g of ammonium ferrous sulphate in a mixture of 20 mL of water and 1 mL of dilute sulphuric acid.

2. Oxalic acid solution: Dissolve 5 g of oxalic acid in 100 mL of water

3. Potassium oxalate solution: Dissolve 2 g of potassium sulphate in 10 mL of water.

4. Hydrogen peroxide solution, 6% (20 volume).

PROCEDURE

Dissolve 2 g of ammonium ferrous sulphate in a mixture of 20 mL of warm water and 1 mL of dilute sulphuric acid in a 100 mL beaker. Add to this with stirring, 25 mL of 5 % aqueous solution of oxalic acid. Heat the contents of the beaker slowly until the solution starts boiling; stop heating after a while and allow the yellow precipitate of ferrous oxalate to settle. Decant the supernatant liquid and add 15 mL of hot water to the precipitate, stir and decant.

In a separate 100 mL beaker, dissolve 2.0 g of potassium oxalate in 10 mL of warm water and transfer the ferrous oxalate solid prepared earlier into this beaker. Heat the mixture to about 40 ^{0}C and add to it 10 mL of 6 % (20 volume) hydrogen peroxide in a slow stream, while stirring the mixture with a glass rod and maintaining the temperature at 40 ^{0}C.

Finally, heat the mixture to boiling and dissolve any ferric hydroxide precipitated by adding 20 mL of 5 % aqueous solution of oxalic acid. If any ferric hydroxide still remains, add further quantity of 5 % aqueous solution of oxalic acid until it completely dissolves; the solution should be nearly boiling during the addition of oxalic acid solution. Filter the hot solution into a 100 beaker, redissolve crystals formed if any by boiling and evaporate the filtrate until a slight encrustation appears on the top of the liquid or the volume of the filtrate reduces to about one third of its original volume, whichever is earlier. Stop evaporating, and add 10 mL of rectified spirit down the sides of the beaker such that a separate alcohol layer forms over the aqueous layer. Cover the beaker with a watch glass, keep the beaker in a dark cup board and allow the complex to crystallize slowly. Finally filter the crystals, dry them and report the yield.

$$(NH_4)_2\,Fe\,(SO_4)_2 6H_2O + H_2C_2O_4 \longrightarrow \underset{\textit{Yellow ppt.}}{FeC_2O_4\downarrow} + (NH_4)_2\,SO_4 + H_2\,SO_4 + 6H_2O$$

$$\underset{\textit{Yellow ppt.}}{4\,FeC_2O_4} + 2\,H_2O_2 + 2\,H_2O + 3\,K_2C_2O_4 \longrightarrow \underset{\textit{Green complex}}{2\,K_3[Fe(C_2O_4)_3]} + \underset{\textit{Reddish brown ppt.}}{2Fe(OH)_3\downarrow} + H_2C_2O_4$$

$$\underset{\textit{Reddish brown ppt.}}{2Fe(OH)_3\downarrow} + 3\,H_2C_2O_4 + 3K_2C_2O_4 \longrightarrow \underset{\textit{Green complex}}{2\,K_3[Fe(C_2O_4)_3]} + 6\,H_2O$$

The compound is photo sensitive. Hence preserve it in a dark cupboard.

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6. Preparation of hexaamminecobalt(III) chloride $[Co(NH_3)_6]\ Cl_3$

PROCEDURE

Place 0.5 g of decolourising charcoal in a 100 mL beaker and add to it a hot solution containing 4.5 g of cobalt(II) chloride and 3.0 g of ammonium chloride in 5 mL of water followed by 10 mL of concentrated ammonia solution. Stir the mixture well. Cool the mixture under a cold water tap and, after cooling, add to it 10 mL of 6 % (20 Volume) hydrogen peroxide taken in a burette drop wise, while stirring the mixture with a glass rod. Heat the mixture to 60 ^{0}C and maintain the same temperature for 15 to 20 minutes, until the pink colour of the solution disappears completely. Cool the mixture under cold water tap and then in ice cold water. Filter the mass and transfer the precipitate on the filter paper into a 100 mL beaker containing a boiling solution of 1.5 mL of concentrated hydrochloric acid in 40 mL of water. When the entire solid except the charcoal has dissolved, filter the hot suspension. Add 5 mL of concentrated hydrochloric acid to the hot filtrate, mix well and cool the solution in the beaker in ice. Filter the crystals, dry and report the yield.

$$CoCl_2 + NH_4Cl + NH_4OH \xrightarrow[H_2O_2]{\text{Charcoal}} [Co(NH_3)_6]\ Cl_3$$

Orange yellow complex

The complex is very stable and consists of a complex cation, $[Co(NH_3)_6]^{3+}$ and three simple anions, $3Cl^-$. In the complex cation, the six NH_3 ligands are octahedrally distributed around central Co(III).

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II. TITRIMETRIC ANALYSIS

1. Determination of Sodium Carbonate in Soda Ash

Discussion: Anhydrous Na_2CO_3, known as soda ash, is a salt formed from H_2CO_3, a very weak acid and NaOH, a strong base. Hence, Na_2CO_3 readily undergoes hydrolysis as

$$Na_2CO_3 + 2\,H_2O \longrightarrow 2\,NaOH + H_2CO_3$$

In essence, determination of Na_2CO_3 with a strong acid is a neutralization type of chemical reaction. In this reaction, two moles of HCl are consumed for one mole of Na_2CO_3 neutralised; in fact, the base liberated by the hydrolysis of Na_2CO_3 is neutralised with HCl.

$$2\,HCl + Na_2CO_3 \longrightarrow 2\,NaCl + H_2O + CO_2 \uparrow$$

Methyl orange is used as an internal indicator in this titration and its colour transition from yellow to orange red takes place in the pH-range of 3.1 to 4.4; the indicator exhibits yellow colour in media having pH greater than 4.4 and pink colour in media having pH less than 3.1. As the pH-transition of the said titration at the equivalence point also comes within this range, methyl orange suites as an internal indicator in the present context.

Solutions and Reagents

1. Standard Na_2CO_3 solution (0.1 N): Dissolve 1.325 g of AR grade Na_2CO_3 (Eq. Wt. 53) in distilled water in a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

2. HCl solution (0.1 N): Add 2.3 mL of concentrated hydrochloric acid to 247 mL of distilled water taken in a 400 mL beaker and homogenise. Transfer the solution into a clean 250 mL volumetric flask and shake well.

3. Soda ash sample solution: Make up the sample solution given in the 100 mL volumetric Flask to the mark with distilled water and homogenise.

4. Methyl orange indicator solution: Dissolve 50 mg of the substance in 100 mL of distilled water.

PROCEDURE

PART - A: ***Standardisation of Hydrochloric Acid Solution Using Standard Sodium Carbonate Solution***. Wash all the given glass apparatus thoroughly with tap water, rinse with distilled water and throw out the washings and rinsings into the sink. Rinse the burette first with the hydrochloric acid solution and then fill it with the same solution up to the zero mark without any air bubbles. Clamp the burette to burette stand. Rinse the 20 mL pipette thoroughly with the standard sodium carbonate solution and pipette out 20 mL of the same solution into a clean 250 mL conical flask. Add 20 mL of distilled water to the solution in the conical

flask using a 50 mL measuring jar. Add two drops of methyl orange indicator to the solution. The solution attains yellow colour at this stage. Titrate the contents of the conical flask against the hydrochloric acid solution taken in the burette. Continue the titration until the colour of the solution in the conical flask changes from yellow to orange red, which marks the end point of the titration. Note down the burette readings to the nearest 0.05 mL and record them in Table-A. Repeat the titrations with fresh 20 mL aliquots of standard sodium carbonate solution, following the above procedure, until two successive titers are concordant. Enter the data in Table-A and calculate the concentration of hydrochloric acid solution as shown under the Table.

Table-A: Standardisation of hydrochloric acid solution using standard sodium carbonate solution

S. No.	Volume of sodium carbonate solution pipetted out, mL V_1	Burette readings, mL		Volume of hydrochloric acid solution rundown from burette, mL V_2
		Initial	Final	
1	20.00			
2	20.00			
3	20.00			

CALCULATIONS: Calculate the concentration of hydrochloric acid solution making use of the formula: $V_1N_1 = V_2N_2$ where

V_1= Volume of sodium carbonate solution pipetted out = 20.00 mL

V_2 = Volume of hydrochloric acid solution rundown from burette = mL

N_1 = Normality of standard sodium carbonate solution = 0.1000 and

N_2 = Normality of hydrochloric acid solution =

As V_1, V_2 and N_1 are known, calculate normality of hydrochloric acid solution as $N_2 = \frac{V_1N_1}{V_2}$

Therefore, the concentration of hydrochloric acid solution, N_2 = N

PART - B: ***Determination of Sodium carbonate in the Given Soda Ash Sample Solution.*** Make up the soda ash sample solution, given in 100 mL volumetric flask, to the mark with distilled water. Homogenize the solution thoroughly by shaking the flask, after closing the volumetric flask with its lid. Fill the burette with the standardized hydrochloric acid solution up to the zero mark and clamp it to the burette stand. Rinse the 20 mL pipette with the given soda ash sample solution twice. Pipette out 20 mL of the same solution into a clean 250 mL conical flask and add 20 mL of distilled water by means of a measuring jar. Also add 2 drops of methyl orange indicator. The solution is yellow in colour at this stage. Titrate the contents of the conical flask against the hydrochloric acid solution taken in the burette. Continue the titration until the colour of the solution in the conical flask changes from yellow to orange red, which marks the end point. Note down the readings of the burette to the nearest 0.05 mL and record them in table-B. Repeat the titrations with fresh 20 mL aliquots of the solution until two successive titers are concordant. Record the results in

Table–B and calculate the concentration and amount of sodium carbonate in the given sample of soda ash solution as shown under Table–B.

Table-B: Determination of sodium carbonate in the given soda ash sample

S. No.	Volume of soda ash sample solution pipetted out, mL V_3	Burette readings, mL		Volume of hydrochloric acid solution rundown from burette, mL V_2^{I}
		Initial	Final	
1	20.00			
2	20.00			
3	20.00			

CALCULATIONS: Calculate the strength of sodium carbonate in the soda ash sample by making use of the formula,

$V_2^{I} N_2 = V_3 N_3$ where,

V_2^{I} =Volume of HCl consumed for 20.00 mL of soda ash sample solution = mL
V_3 =Volume of soda ash sample solution pipetted out = 20.00 mL
N_2 =Normality of hydrochloric acid = (PART – A) and
N_3 = Normality of sodium carbonate in the soda ash sample solution, which can be calculated as V_2^{I}, N_2 and V_3 are known.

Therefore, $N_3 = V_2^{I} N_2 / V_3$ =

The strength of sodium carbonate in the soda ash sample solution, N_3 = N

Amount of Na_2CO_3 in the given sample (100 mL) = $\frac{N_3 \times (\text{Eq.Wt. of } Na_2CO_3) \times 100}{1000} = \frac{N_3 \times 53}{10}$

$= N_3 \times 5.3$ = g

REPORT: Determination of Na_2CO_3 in the given soda ash sample.

Roll/Regd. Number	Amount of Na_2CO_3, g		% Error
	Given	Reported	

Percentage of Error = $\frac{(\text{Amount Given} - \text{Amount Reported}) \times 100}{\text{Amount Given}}$ =

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2. Determination of Iron(II) by Potassium Dichromate Method

Discussion: The reaction between $K_2Cr_2O_7$ and iron(II) is an example for a redox reaction. In the presence of H_2SO_4, $K_2Cr_2O_7$ oxidises iron(II) to iron(III) and chromium(VI) in dichromate gets reduced to chromium(III) state.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O)$$

$$6FeSO_4 + 3H_2SO_4 + 3(O) \longrightarrow 3Fe_2(SO_4)_3 + 3H_2O$$

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow K_2SO_4 + 3Fe_2(SO_4)_3 + 7H_2O$$

According to the above equation, 1 mole of $K_2Cr_2O_7$ reacts with 6 moles of $FeSO_4$. To locate the end point, Diphenylamine (DPA) is used as internal indicator. Even though the reaction is spontaneous, premature end points result due to the closeness of redox potential of the indicator system to that of Fe(III)/Fe(II) system. However, correct end point can be achieved by adding syrupy phosphoric acid to the reaction mixture; phosphoric acid binds ferric iron as phosphato complex and lowers the concentration of free Fe(III) in solution and thereby lowers the redox potential of Fe(III)/Fe(II) system considerably (Recollect Nernst's Equation). This results in the redox potential of the indicator system to lie much above that of the iron system, thus preventing premature end points. Therefore, in the presence of H_3PO_4, once all the iron(II) ions react completely with dichromate, the next drop of dichromate solution oxidises the indicator and the oxidised form of the indicator is blue violet in colour. Hence the colour transition at the end point is from green to gray green to blue violet. As potassium dichromate is a primary standard substance, it's standard solution is prepared by directly weighing the required amount of it in a known volume of distilled water and utilised to determine iron(II) in the given problem solution.

Solutions and Reagents

1. Standard potassium dichromate solution (0.10 N): Dissolve 1.226 g of AR $K_2Cr_2O_7$ (Eq. Wt. 49.04) in distilled water in a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise the solution.

2. Iron(II) solution (0.1 N): Weigh out 9.8 g of ammonium ferrous sulphate hexahydrate, $(NH_4)_2Fe(SO_4)_2\,6H_2O$ into a clean 400 mL beaker and dissolve it in a mixture of 150 mL of water and 50 mL of 5N sulphuric acid. Transfer the solution into a 250 mL volumetric flask, make up the solution up to the mark with distilled water and homogenise.

3. Dilute sulphuric acid solution (5 N): Carefully add, in small portions, 70 mL of AR concentrated sulphuric acid to 400 mL of distilled water taken in a 1000 mL beaker. Allow the hot solution to cool to room temperature, make up the volume to 500 mL with distilled water and homogenise.

4. Syrupy phosphoric acid (H_3PO_4) (85 %): Use the acid strait away***.***

5. Diphenylamine (DPA) Indicator: Dissolve 1 g of the substance in 100 mL of concentrated sulphuric acid taken in a 250 mL beaker. Finally transfer the liquid into a properly labeled reagent bottle.

PROCEDURE

Determination of Iron(II) in the Given Solution Using Standard Potassium Dichromate Solution: Wash all the glass apparatus first with tap water and then rinse with distilled water. Rinse the burette with the standard potassium dichromate solution and fill it with the same solution up to the zero mark without any air bubbles. Clamp the burette to its stand. Rinse the 20 mL pipette with the given iron(II)) sample solution thoroughly and pipette out 20 mL of the same solution into a clean 250 mL conical flask. To this add 10 mL of distilled water, 15 mL of 5N sulphuric acid and 3 mL of syrupy phosphoric acid followed by 2 drops DPA indicator. Titrate the colourless solution in the conical flask against standard potassium dichromate solution taken in the burette until the colour of the solution changes from green to gray green. Then add the standard potassium dichromate solution slowly, in drops until the first tinge of blue violet, which remains permanent on shaking appears. Note down the burette readings to the nearest 0.05 mL and record them in Table–A. Repeat the titrations with 20 mL aliquots of iron(II) solution until two successive concurrent titers are obtained and enter the readings in the same table. Calculate the concentration of iron(II) as shown under Table-A.

Table - A: Determination of iron(II) using standard potassium dichromate solution

S. No.	Volume of iron(II) solution pipetted out, mL V_2	Burette readings, mL		Volume of potassium dichromate solution rundown from burette, mL V_1
		Initial	Final	
1.	20.00			
2.	20.00			
3.	20.00			

CALCULATIONS: Calculate the concentration of iron(II) using the equation,

$$N_1V_1 = N_2V_2 \quad \text{where}$$

N_1 = Normality of standard potassium dichromate solution =

V_1 = Volume of standard potassium dichromate solution rundown from burette= mL

V_2 = Volume of iron(II) solution pipetted out = 20.00 mL and

N_2 = Normality of iron(II)solution.

Since N_1, V_1, and V_2 are known, calculate the normality of iron(II) in the solution as

$$N_2 = \frac{N_1 V_1}{V_2} =$$

Therefore, Normality of iron(II) in the solution N_2 =

Finally calculate the amount of iron(II) present in the given 100 mL sample solution using the formula

$$\frac{N_2 \times (\text{Eq. Wt. of iron(II)}) \times 100}{1000} = \frac{N_2 \times 55.85}{10} = 5.585 \times N_2 = \quad \text{g}$$

REPORT: The amount of iron(II) in the given sample solution is _____ g.

Roll/Regd. No.	Amount of iron(II), g		% Error
	Given	Reported	

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3. Determination of Iron(II) by Potassium Permanganate Method

Discussion: Reaction between $KMnO_4$ and iron(II) is an example of a redox reaction where Mn(VII) in $KMnO_4$ oxidises iron(II) to iron(III) and itself gets reduced from Mn(VII) to Mn(II) state. The titration is carried out in dilute sulphuric acid medium.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5\,(O)$$

$$10FeSO_4 + 5H_2SO_4 + 5\,(O) \longrightarrow 5\,Fe_2(SO_4)_3 + 5H_2O$$

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

According to the above equation, 2 moles of $KMnO_4$ react with 10 moles of $FeSO_4$. As potassium permanganate is not a primary standard, its solution has to be standardised using a standard solution like that of oxalic acid solution.

The reaction between oxalic acid and potassium permanganate is also a redox reaction. In this reaction, $KMnO_4$ acts as an oxidising agent, which oxidises $H_2C_2O_4$ to CO_2 and in the process Mn(VII) gets reduced to Mn(II) state.

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2 \uparrow$$

According to the above reaction, 2 moles of $KMnO_4$ react with 5 moles of $H_2C_2O_4$. As the reaction is very slow at room temperature, it is initiated at a temperature of 70 – 80 ^oC. Even then, the rate of reaction is initially slow, it gets efficiently catalysed by the *in-situ* generated Mn^{+2} ions in the solution; Mn^{+2} acts as an auto-catalyst in the reaction. So, as the titration progresses, the reaction picks up speed. Usually, in permanganametry, the self colour of $KMnO_4$ is used to locate the end point.

Solutions and Reagents

1. Standard Oxalic Acid Solution (0.10 N): Dissolve 1.575 g of AR $H_2C_2O_4\,2H_2O$ (Eq. Wt. 63.04) in distilled water in a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

2. Potassium permanganate solution (0.1 N): Dissolve 0.8 g of $KMnO_4$ solid (Eq. Wt. 31.6) in *260 mL* distilled water in a 400 mL beaker and heat to boiling. Cool the solution to room temperature, filter through glass wool into an amber coloured bottle and preserve.

3. Iron(II) solution (0.1 N): Weigh out 9.8 g of ammonium ferrous sulphate hexahydrate, $(NH_4)_2\,Fe(SO_4)_2\,6H_2O$ into a clean 400 mL beaker and dissolve it in a mixture of 150 mL of water and 50 mL of 5N sulphuric acid. Transfer the solution into a 250 mL volumetric flask, make up the solution up to the mark with distilled water and homogenise.

4. Dilute sulphuric acid solution (5 N): Carefully add, in small portions, 70 mL of AR concentrated sulphuric acid to 400 mL of distilled water taken in a 1000 mL beaker. Allow the hot solution to cool to room temperature, make up the volume to 500 mL with distilled water and homogenise.

PROCEDURE

PART – A: ***Standardisation of Permanganate Solution Using Standard Oxalic Acid Solution.***
Wash all the glass apparatus first with tap water and then rinse with distilled water. Rinse the burette with potassium permanganate solution and fill it with the same solution up to the zero mark, avoiding air bubbles. Rinse the 20 mL pipette with standard oxalic acid solution thoroughly and pipette out 20 mL of the same solution into a clean 250 mL conical flask. To this add 20 mL each of 5N sulphuric acid solution and 10 ml of distilled water. Heat the contents of the conical flask to a temperature of about 70 – 80 ^{o}C (appearance of first few bubbles in the solution). Stop the heating and titrate the contents of the conical flask in the hot condition against potassium permanganate solution taken in the burette until the colour of the solution in the conical flask changes from colourless to permanent pale pink ***(Note: Initially, the reaction is slow and hence the next drop of permanganate is to be added only after the colour due to the earlier drop is completely discharged).*** Note down the burette readings to the nearest 0.05 mL and record them in Table – A. Repeat the above process, each time pipetting 20 mL aliquots of standard oxalic acid solution, until two successive concurrent titers are obtained. Enter the data in Table-A and calculate the concentration of permanganate solution, as shown under Table-A.

Table-A: Standardisation of potassium permanganate solution using standard oxalic acid solution

S. No.	Volume of oxalic acid solution pipetted out, mL V_1	Burette readings, mL		Volume of permanganate solution rundown from burette, mL V_2
		Initial	Final	
1.	20.00			
2.	20.00			
3.	20.00			

CALCULATIONS: Calculate the concentration of permanganate solution using the equation,

$$N_1V_1 = N_2V_2 \quad \text{where,}$$

N_1 = Normality of standard oxalic acid solution =
V_1 = Volume of oxalic acid solution pipetted out = 20.00 mL
V_2 = Volume of permanganate solution rundown from burette = mL and
N_2 = Normality of permanganate solution
As N_1 , V_1 and V_2 are known, calculate the normality of permanganate, N_2 as

$$N_2 = \frac{N_1V_1}{V_2} =$$

Normality of $KMnO_4$ solution N_2 =

PART – B: ***Determination of Iron(II) in the Given Sample solution Using Standard Potassium Permanganate Solution.*** Make up the given iron(II) sample solution in 100 mL volumetric flask to the mark with distilled water and homogenise it properly. Fill the burette with potassium permanganate solution and clamp it to the burette stand. Wash the 20 mL pipette first with distilled water and then rinse with iron(II) sample solution thoroughly and pipette out 20 mL of the solution into a clean 250 mL conical flask. To this add 20 mL of distilled water and 20 mL of 5N sulphuric acid solution. Titrate the contents of the conical flask directly against potassium permanganate solution **(No heating is necessary)** until the colour of the solution in the conical flask changes from colourless to permanent pale pink. Note down the burette readings to the nearest 0.05 mL and record them in Table-B. Repeat the titrations with fresh 20 mL aliquots of iron(II) sample solution until two successive concurrent titers are obtained. Enter the results in Table–B and calculate the concentration and amount of iron(II) in the sample solution as shown under the Table – B.

Table-B: Determination of iron(II) using standard potassium permanganate solution

S. No.	Volume of iron(II) sample solution pipetted out, mL V_3	Burette Readings, mL		Volume of permanganate solution rundown from burette, mL V_2^I
		Initial	Final	
1.	20.00			
2.	20.00			
3.	20.00			

CALCULATIONS: Calculate the concentration of iron(II) in the sample solution using the equation

$$N_2V_2^1 = N_3V_3$$ where

N_2 = Normality of the permanganate solution (Part – A) =

V_2^I = Volume of the permanganate solution rundown from burette (Part – B) = mL

V_3 = Volume of iron(II) sample solution pipetted out = 20.00 mL and

N_3 = Normality of iron(II) in sample solution.

As N_2, V_2^I and V_3 are known, calculate the concentration of iron(II) as $N_3 = N_2 V_2^I / V_3$ =

Finally, calculate the amount of iron(II) present in the given sample of 100 ml using the equation,

$$\frac{N_3 \times (\text{Eq. Wt. of Fe(II)}) \times 100}{1000} = \frac{N_3 \times 55.85}{10} = \quad g$$

REPORT: Amount of iron(II) present in the given 100 ml sample solution _____ g

Roll/Regd. Number	Amount of iron(II), g		% Error
	Given	Reported	

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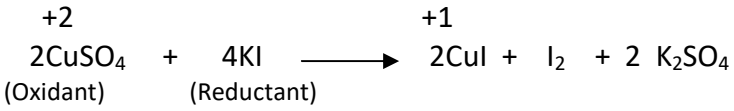
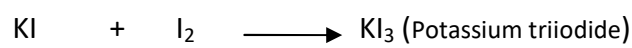
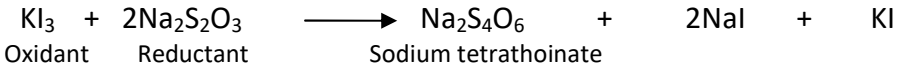
4. Determination of Copper(II) by Sodium Thiosulphate Method

Discussion: Copper(II) in solution cannot be directly titrated with sodium thiosulphate(hypo) solution as there is no direct reaction between copper(II) (oxidant) and hypo (reductant). However, in neutral solution, copper(II) can directly oxidize iodide to iodine which, in turn, can oxidize hypo quantitatively. Therefore, copper(II) is indirectly determined iodometrically by adding potassium iodide solution to copper(II) solution and titrating the liberated iodine with hypo solution, provided the copper(II) solution is free from mineral acid. The basic reactions involved are:







According to the above equation, two equivalents of $CuSO_4$ liberate two equivalents of molecular iodine, which in turn oxidize two equivalents of $Na_2S_2O_3$. If free mineral acid is present as impurity in the copper(II) solution, it causes interference in the above reaction; in the presence of mineral acids, iodide gets oxidised to iodine by the dissolved oxygen present in the medium. However, the above interference can be overcome by adding a small amount of Na_2CO_3 and dissolving the precipitated copper carbonate in dilute acetic acid; sodium carbonate neutralizes the mineral acid and the slight excess of carbonate causes precipitation of a small amount of $CuCO_3$ which readily dissolves in dilute acetic acid (a weak acid). As sodium thiosulphate (Hypo) is not a primary standard, its solution has to be standardized with a primary standard solution like that of potassium iodate. But, as copper(II) in the sample is to be determined, to avoid methodical error, a standard solution of copper(II), prepared from Analytical Reagent grade $CuSO_4.5H_2O$ (a secondary standard substance) is used to standardize Hypo solution.

Solutions and Reagents

1. Standard copper sulphate solution (O.10 N): Dissolve 2.497 g of AR $CuSO_4\ 5H_2O$ (Eq. Wt. 249.7) in distilled water in a 100 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

***2*. Sodium thiosulphate (hypo) (0.1 N):** Dissolve 6.2 g of $Na_2S_2O_3\ 5H_2O$ (Eq. Wt. 248.2) in distilled water in a 250 mL volumetric flask and add about 0.1 g of Na_2CO_3 to it. Make up the solution to the mark with distilled water and homogenise. Keep the solution in the dark, whenever it is not in use.

3. Potassium iodide solution (10 %): Dissolve 10 g of iodate free potassium iodide solid in 100 mL of distilled water.

4. Starch indicator solution (1 %): Weigh about 1 g of soluble starch on to a watch glass and make it into a slurry with distilled water. Heat to boiling 100 mL of distilled water in a 250 mL beaker and transfer the slurry into the boiling water and stir the water with a glass rod until the solution becomes almost clear. Cool and make use of the solution as an internal indicator.

PROCEDURE

PART – A: ***Standardisation of Thiosulphate Solution Using Standard Copper Sulphate Solution:***

Wash all the given glass apparatus with tap water and then rinse with distilled water. Rinse the burette with hypo solution and fill it with the same solution up to the zero mark avoiding air bubbles and clamp the burette to its stand. Make up the standard copper(II) solution up to the mark with distilled water and homogenise. Rinse the 20 mL pipette with standard copper(II) solution thoroughly and pipette out 20 mL of the same solution into a clean 250 mL iodine flask. Add to that 10 mL of 10 % KI solution. The solution becomes dark brown in colour due to the liberation of iodine. Add 40 ml of distilled water down the sides of the flask, immediately close the flask with its lid and then allow it to stand for about two minutes to ensure complete liberation of iodine. A small quantity of distilled water may also be added over the lid. After **2** minutes, take out the lid and allow the water to rundown along the walls of the iodine flask. Titrate the brown coloured mass in the iodine flask against hypo solution taken in the burette until it becomes straw yellow in colour. Then add 2 mL of starch indicator. The mass in the iodine flask now attains blue or violet colour. Continue the titration with hypo until the blue colour disappears sharply with one drop addition of hypo. Note down the burette readings to the nearest 0.05 mL and recorded them in Table-A. Continue the above procedure with fresh 20 mL aliquots of copper(II) solution until two successive concurrent titers are obtained and enter the readings in Table - A.

Table-A: Standardisation of hypo solution with standard copper(II) solution.

S. No.	Volume of copper(II) solution pipetted, mL V_1	Burette readings, mL		Volume of hypo solution run down from burette, mL V_2
		Initial	Final	
1 2 3	20.00 20.00 20.00			

CALCULATIONS: Calculate the concentration of hypo solution using the equation,

$V_1N_1 = V_2N_2$ where

V_1 = Volume of standard copper(II) solution pipetted out = 20.00 mL

N_1 = Normality of standard copper(II) solution =

V_2 = Volume of hypo solution rundown form burette = mL and

N_2 = Normality of hypo solution

Calculate the normality of hypo solution, N_2 by substituting the known values of N_1, V_1 and V_2 in the equation, $N_2 = V_1 N_1 / V_2$

Concentration of Hypo solution, N_2 = N

PART – B: ***Determination of Copper(II) in Problem Solution Using Standard Hypo Solution:***
Make up the given copper(II) sample solution in the volumetric flask up to the mark by adding distilled water and homogenise. Fill the burette with the hypo solution up to the zero mark avoiding air bubbles and clamp the burette to its stand. Pipette down 20 mL of copper(II) problem solution into a clean 250 mL iodine flask, after initially rinsing the pipette with the problem solution twice. Add into the iodine flask 10 ml of 10% KI solution, immediately followed by 40 ml of distilled water down the walls of the flask and close the flask with its lid. Add a small quantity of distilled water over the lid of the iodine flask and allow the reaction to complete by giving **2** minutes time. After two minutes, take out the lid and allow the water to rundown along the walls of the iodine flask. Then titrate the brown coloured mass against hypo solution until it attains straw yellow colour. At this stage add 2 mL of starch indicator and continue the titration with hypo solution until the blue colour gets discharged with just 1 drop of hypo. Note down the burette readings to the nearest 0.05 mL and record them in Table–B. Continue the above procedure with 20 mL aliquots of sample solution until two successive concurrent titers are obtained and enter the readings in Table-B.

Table-B: Determination of copper(II) in the given problem solution

S. NO.	Volume of problem solution pipetted out, mL V_3	Burette readings, mL		Volume of hypo solution rundown from burette, mL V_2^{I}
		Initial	Final	
1 2 3	20.00 20.00 20.00			

CALCULATIONS : Calculate the concentration of copper(II) in the problem solution using the formula

$V_2^{I} N_2 = V_3N_3$ where

V_2^{I} = Volume of hypo solution rundown from burette (Part – B) =

N_2 = Normality of hypo solution (Part – A) =

V_3 = Volume of copper(II) (problem)solution pipetted out =20.00 mL and
N_3 = Normality of copper(II) in the problem solution

As N_2, V_2^I and V_3 are known, calculate the concentration of copper(II) in the problem solution as

$$N_3 = V_2^I N_2 / V_3 = \quad N$$

Finally, calculate the amount of copper(II) present in the problem solution using the formula,

$$\frac{N_3 \times (\text{Eq.Wt. of Cu(II)}) \times 100}{1000} = \frac{N_3 \times 63.55}{10} = 6.355 \times N_3 =$$

REPORT: The amount of copper(II) present in the sample solution is g.

Roll/Regd. No.	Amount of copper(II), g		% Error
	Given	Reported	

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5. Determination of Zinc(II) by Potassium Ferrocyanide Method

Discussion: Zinc(II) ions in acid or neutral medium react with potassium ferrocyanide solution to form very sparingly soluble $K_2Zn_3[Fe(CN)_6]_2$.

$$3\ ZnSO_4 + 2\ K_4[Fe(CN)_6] \longrightarrow K_2Zn_3[Fe(CN)_6]_2 \downarrow + 3\ K_2SO_4$$

This precipitation reaction forms the basis for the titrimetric determination of zinc with standard potassium ferrocyanide; zinc ions in 2 N sulphuric acid medium, taken in the conical flask, are directly titrated with standard potassium ferrocyanide solution taken in a burette using diphenylamine as internal indicator. Interestingly, even though basically it is a precipitation reaction, a redox indicator is utilized to locate the end point of the titration. The functioning of the redox indicator, diphenylamine, in the precipitation titration can be readily explained basing on the modified Nernst equation,

$$E = E^0 + 0.0591 \log_{10} [\{Fe(CN)_6\}^{3-}] / [\{Fe(CN)_6\}^{4-}]$$

where $[\{Fe(CN)_6\}^{3-}]$ and $[\{Fe(CN)_6\}^{4-}]$ stand for the concentrations of ferricyanide and ferrocyanide respectively. During the course of the titration, as long as zinc ions are available in solution, $[\{Fe(CN)_6\}^{4-}]$ is very low in solution and the redox potential is large enough to oxidize diphenylamine, imparting blue violet colour to the solution. As soon as the zinc ions are quantitatively precipitated (not available in solution), the next drop of the ferrocyanide solution added from the burette causes a sudden increase in $[\{Fe(CN)_6\}^{4-}]$ in solution (the denominator in the log factor increases very significantly) and hence a sudden decrease in the redox potential. As the potential now developed is much lower than the redox potential of the indicator system, the violet blue coloured oxidized form of the indicator gets reduced back to colourless diphenylamine, thus facilitating the location of the end point of the titration.

Solutions and Reagents

1. ***Standard zinc sulphate solution (0.05 M):*** Dissolve 3.594 g of AR $ZnSO_4\ 7H_2O$ (M.Wt. 287.54) in distilled water in a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

2. ***Potassium ferrocyanide solution (0.05 N):*** Dissolve 5.28 g of AR $K_4[Fe(CN)_6]$ (M.Wt. 422.42) And about 0.1 g of potassium ferricyanide, $K_3[Fe(CN)_6]$ in distilled water in a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

3. ***Dilute sulphuric acid (5 N):*** Carefully add, in small portions, 70 mL of AR concentrated sulphuric acid to 400 mL of distilled water taken in a 1000 mL beaker. Allow the hot solution to cool to room temperature, make up the volume to 500 mL with distilled water and homogenize.

4. 10 % Ammonium sulphate solution: Dissolve 10 g of ammonium sulphate in 100 mL of distilled water.

5. Diphenylamine (DPA) Indicator: Dissolve 1 g of the substance in 100 mL of concentrated sulphuric acid taken in a 250 mL beaker and stir the acid. Finally transfer the liquid into a properly labeled reagent bottle.

Procedure

PART – A: ***Standrdisation of Potassium Ferrocyanide Solution with Standard Zinc Sulphate Solution.*** Wash all the glass apparatus with tap water and rinse with distilled water. Rinse the burette with potassium ferrocyanide solution and fill it with the same solution up to the zero mark, avoiding air bubbles. Clamp the burette to its stand. Rinse the 20 mL pipette with standard zinc sulphate solution thoroughly and pipette out 20 mL of the same solution into a clean 250 mL conical flask. Add to that 30 mL of 5N sulphuric acid, 10 mL of 10 % ammonium sulphate solution and 4 drops of DPA indicator solution. Titrate slowly with vigorous swirling of the contents of the conical flask against potassium ferrocyanide solution taken in the burette until the colour of the solution in the conical flask changes from violt blue to pale green. Note down the burette readings to the nearest 0.05 mL and record them in Table – A. Repeat the above process, each time pipetting 20 mL aliquots of standard zinc sulphate solution, until two successive concurrent titers are obtained. Enter the results in Table-A and calculate the concentration of permanganate as shown under Table-A.

Table-A: Standardisation of potassium ferrocyanide solution with standard zinc sulphate solution.

S. No.	Volume of standard zinc sulphate solution pipetted out, mL V_1	Burette readings, mL		Volume of potassium ferrocyanide solution rundown from burette, mL V_2
		Initial	Final	
1 2 3	20.00 20.00 20.00			

CALCULATIONS: Calculate the concentration of potassium ferrocyanide in the solution by using

the equation,

$$V_1M_1 / 3 = V_2 M_2 / 2 \quad \text{where}$$

V_1 = Volume of standard zinc sulphate solution pipetted out = 20.00 mL
M_1 = Molarity of standard zinc sulphate solution =
V_2 = Volume of potassium ferrocyanide solution rundown form the burette = mL and
M_2 = Molarity of potassium ferrocyanide solution

Calculate the molarity of potassium ferrocyanide solution, M_2 by substituting the known values of M_1, V_1 and V_2 in the equation, $M_2 = 2 V_1 M_1 / 3 V_2$ =

Concentration of potassium ferrocyanide solution, M_2 = M

PART – B: Determination *of Zinc(II) in Problem Solution Using Standardised Potassium Ferrocyanide Solution.* Make up the problem solution given in 100 mL volumetric flask up to the mark with distilled water and hogenise it. Rinse the 20 mL pipette twice with the problem solution and pipette out 20 mL of the same solution into a clean 250 mL conical flask. Add to that 30 mL of 5N sulphuric acid, 10 mL of 10 % ammonium sulphate solution and 4 drops of DPA indicator solution. Titrate slowly with vigorous swirling of the contents of the conical flask against potassium ferrocyanide solution taken in the burette until the colour of the solution in the conical flask changes from blue violet to pale green. Note down the burette readings to the nearest 0.05 mL and record them in Table – B. Repeat the above process, each time pipetting 20 mL aliquots of the problem solution, until two successive concurrent titers are obtained. Enter the results in Table-B and calculate the concentration of zinc(II) as shown under Table-B.

Table - B: Determination of zinc(II) in the given problem solution

S. No.	Vol. of zinc(II) problem solution pipetted out, mL V_3	Burette readings, mL		Vol. of potassium ferrocyanide solution rundown from burette, mL V_2^{I}
		Initial	Final	
1 2 3	20.00 20.00 20.00			

CALCULATIONS: Calculate the concentration of zinc(II) in the given problem solution by using the equation,

$$V_3 M_3 / 3 = V_2^{I} M_2 / 2$$ where

V_2^{I} = Volume of potassium ferrocyanide solution rundown form burette (Part - B)= mL
M_2 = Molarity of potassium ferrocyanide solution as calculated in Part - A
V_3 = Volume of zinc(II) problem solution pipetted out = 20.00 mL and
M_3 = Molarity of zinc(II) in the zinc(II) problem solution =

Calculate the molarity of zinc in the problem solution, M_3 by substituting the known values of M_2, V_3 and V_2^{I} in the equation,

$$M_3 = \frac{3 V_2^{I} M_2}{2 V_3}$$

Concentration of zinc(II) in the problem solution, M_3 = M

Finally, calculate the amount of zinc(II) in the problem solution using the equation,

$$\frac{M_3 \times (\text{At. Wt. of Zn}) \times 100}{1000} = \frac{M_3 \times 65.39}{10}$$

$$= 6.539 \times M_3 =$$

REPORT: The amount of zinc(II) present in the sample solution is g.

Roll/Regd. No.	Amount of zinc(II), g		% Error
	Given	Reported	

Precautions: 1. The titrations must be carried out slowly and with thorough mixing of the mass in the conical flask.

2. The sulphuric acid concentration near the end point must be 1.6 to 2.0 N.

3. In order to get reproducible results, it is essential to maintain uniform conditions in the titrations.

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6. Determination of Ferrocyanide by Ceric Sulphate Method

Discussion: Ferro cyanide in dilute sulphuric acid solution can be determined making use of standard ceric (cerium^{IV}) sulphate solution. Cerium(IV) in sulphuric, or nitric or perchloric acid solution is a powerful oxidizing agent. Its reduction potential in 1 to 8 N sulphuric acid at 25^0 C is about 1.43 V. It is used as a powerful oxidizing agent only in acid solutions, best in 0.5 N or higher acid concentration. The ceric sulphate has dark orange colour in concentrated solutions and yellow colour in more dilute solutions. The cerium(IV) sulphate in concentrated solutions can serve as self indicator but, in more dilute solutions an internal indicator like DPA, NPA or Ferroin has to be used. The basic chemical reaction involved in the process is:

$$[Fe^{II}(CN)_6]^{4-} + Ce^{IV} \longrightarrow [Fe^{III}(CN)_6]^{3-} + Ce^{III}$$

In general, ceric sulphate solutions have to be standardized using standard solution of As_2O_3, $Na_2C_2O_4$ or $K_4Fe(CN)_6$. AR Grade potassium ferrocyanide, $K_4Fe(CN)_6$ is readily available and can be made use of to standardize ceric sulphate solution. As the aim of the experiment is to determine ferrocyanide concentration in the problem solution, methodical error, if any, gets cancelled if standard ferrocyanide is used to standardize the ceric sulphate solution.

Solutions and Reagents

1. ***Standard potassium ferrocyanide solution (0.05 N):*** Dissolve 5.28 g of AR $K_4[Fe(CN)_6]$ (M.Wt. 422.42) in distilled water in a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

2. ***Ceric sulphate solution (0.05 N):*** Dissolve 7.9 g of $(NH_4)_4\ Ce(SO_4)_4\ 2H_2O$ (M.Wt. 632.57) in distilled water in the presence of 50 mL of 5 N H_2SO_4 in a 250 mL volumetric flask. Make up the solution to the mark with distilled water and homogenise.

3. ***Dilute sulphuric acid (5 N):*** Carefully add, in small portions, 70 mL of AR concentrated sulphuric acid to 400 mL of distilled water taken in a 1000 mL beaker. Allow the hot solution to cool to room temperature, make up the volume to 500 mL with distilled water and homogenize.

4. ***N-phenyl anthranilic acid (NPA) indicator:*** Dissolve 0.1 g of the substance in a mixture of 5 mL of 0.1 N NaOH and 95 mL of distilled water.

Procedure

PART – A: ***Standardisation of Ceric Sulphate Solution Using Standard Potassium Ferrocyanide Solution.*** Wash all the glass apparatus with tap water and rinse with distilled water. Rinse the burette with ceric sulphate solution and fill it with the same solution up to the zero mark, avoiding air bubbles and clamp it to its stand. Rinse the 20 mL pipette with

standard potassium ferrocyanide solution thoroughly and pipette out 20 mL of the same solution into a clean 250 mL conical flask. Add to that 20 mL of 5N sulphuric acid and 5 drops of NPA indicator solution. Titrate the contents of the conical flask against ceric sulphate solution taken in the burette until the colour of the solution in the conical flask changes from yellow to orange-red. Note down the burette readings to the nearest 0.05 mL and record them in Table – A. Repeat the above process, each time pipetting 20 mL aliquots of standard potassium ferrocyanide solution, until two successive concurrent titers are obtained. Enter the results in Table-A and calculate the concentration of permanganate as shown under Table-A.

Table-A: Standardisation of ceric sulphate solution with standard ferrocyanide solution.

S. No.	Volume of ferrocyanide solution pipetted out, mL V_1	Burette readings, mL		Volume of cerium(IV) solution rundown from burette, mL V_2
		Initial	Final	
1 2 4	20.00 20.00 20.00			

CALCULATIONS: Calculate the concentration of cerium(IV) by using the equation,

$V_1N_1 = V_2N_2$ where

V_1 = Volume of standard ferrocyanide solution pipetted out = 20.00 mL

N_1 = Normality of standard ferrocyanide solution =

V_2 = Volume of cerium(IV) solution rundown form burette = mL and

N_2 = Normality of cerium(IV) in solution

Calculate the normality of cerium(IV) in solution , N_2 by substituting the known values of N_1, V_1 and V_2 in the equation, $N_2 = V_1 N_1 / V_2$

Concentration of cerium(IV) in solution, N_2 = N

PART - B*. Determination of Ferrocyanide in the Given Sample Solution Using Standard Ceric Sulphate Solution:* Make up the given problem solution in the volumetric flask up to the mark with distilled water and homogenise. Rinse the 20 mL pipette with the problem solution twice. Pipette down 20 mL of the solution into a clean 250 mL conical flask and proceed exactly following the procedure as described in the above standardisation part. Basing on the concentration of ceric sulphate calculated in the standardization part, find out the strength and amount of ferrocyanide in the problem solution as shown under Table-B.

Table - B: Determination of ferrocyanide with standard ceric sulphate solution.

S. No.	Volume of problem solution pipetted out, mL V_3	Burette readings, mL		Volume of cerium(IV) solution rundown from burette, mL V_2^{I}
		Initial	Final	
1 2 3	20.00 20.00 20.00			

CALCULATIONS: The concentration of ferrocyanide solution can be calculated using the equation, $V_3N_3 = V_2^{I}N_2$ where

V_2^{I} = Volume of cerium(IV) solution rundown form the burette (Part – B)= mL
N_2 = Normality of cerium(IV) solution (Part – A) =
V_3 = Volume of ferrocyanide problem solution pipetted out = 20.00 mL and
N_3 = Normality of ferrocyanide in the problem solution

Calculate the normality of ferrocyanide solution, N_3 in the problem solution by substituting the known values of N_2, V_3 and V_2^{I} in the equation, $N_3 = V_2^{I} N_2 / V_3$

Concentration of $K_4Fe(CN)_6$ in the problem solution, N_3 = N

Finally, calculate the amount of $K_4Fe(CN)_6$ present in the given sample by using the formula,

$$= \frac{N_3 \times (\text{Eq.Wt. of } K_4Fe(CN)_6) \times 100}{1000} = \frac{N_3 \times 422.42}{10} = 42.24 \times N_3 =$$

REPORT: The amount of $K_4Fe(CN)_6$ present in the given problem solution is g.

Roll/Regd. No.	Amount of $K_4Fe(CN)_6$, g		% Error
	Given	Reported	

Precautions: 1. The overall concentration of sulphuric acid in the ceric sulphate solution has to be 0.5 N or higher

2. The ferrocyanide solution has to be prepared in distilled water.

3. The sulphuric acid concentration at the end point of the titration should be at least 1.6 N.

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COMPLEXOMETRIC TITRATIONS USING EDTA

Discussion: **E**thylene**d**iamine**t**etra-**a**cetic acid, EDTA is a versatile complexing agent. It forms 1:1 complexes of varying stability with different metal ions, in aqueous solution. The stabilities of the complexes formed by EDTA depend not only on the nature of the metal ion but also on pH of the medium, thus enhancing the application of EDTA for metal ion analysis. Compared to EDTA, its disodium salt is more soluble in water and finds wider application as a titrimetric reagent. Moreover, indicators used in EDTA titrations also form pH – dependent dark coloured complexes with metal ions and serve as metal ion indicators. As the Metal - indicator complex is much less stable than the corresponding Metal – EDTA complex, EDTA displaces the indicator from Metal – Indicator complex and liberates the free indicator. The fact that the Metal - indicator complex exhibits a different colour from that of the free indicator and that it is less stable than the Metal – EDTA complex is utilized in detecting the end point in the EDTA titrimetry.

$$\text{Metal - Indicator complex} + \text{EDTA} \xrightarrow{\textit{Buffer}} \text{Metal – EDTA complex} + \text{Indicator}$$

Maintenance of pH of the medium is very critical in many EDTA titrations; often the pH should not vary beyond $\pm$ 1 unit of pH (better if it is within $\pm$ 0.5) from the recommended pH to get good results.

7. Determination of Zinc(II) by EDTA Method

Discussion: Zinc(II) reacts with EDTA forming a stable and colourless 1 : 1 complex. An accurate and most convenient complexometric titration of zinc(II) with EDTA is possible at pH – 10, using Eriochrome Black T (EBT) as metal ion indicator, to detect the end point. In the titration of zinc with EDTA, as usual, a very small quantity of the indicator compared to that of zinc(II) is added to the analyte solution. So, initially a wine red coloured Zn – EBT complex forms which is in equilibrium with excess of free zinc(II) ions. As the titration with EDTA continues, colourless Zn – EDTA complex starts accumulating in the solution and this continues up to the end point where all the free zinc(II) ions are complexed with EDTA. Once this happens, the next drop of EDTA added attacks the wine red coloured Zn – EBT complex forming more stable Zn – EDTA complex and setting the EBT indicator free, which is blue in colour under the conditions. Hence the end point of the titration is marked by a sudden colour change from wine red to blue. The situation near the end point of the titration can be depicted as

$$\underset{\textit{Colourless}}{\text{Zn(II)}} + \underset{\textit{Blue}}{\text{EBT}} \xrightarrow{\textit{pH-10}} \underset{\textit{(Wine-red coloured \& less stable complex)}}{\text{Zn(II) - EBT}} \xrightarrow{\textbf{EDTA}} \underset{\textit{(Colourless \& more stable complex)}}{\text{Zn(II) - EDTA}} + \underset{\textit{Blue}}{\text{EBT}}$$

Solutions and Reagents

1. Standard zinc sulphate solution (0.05 M): Dissolve 3.594 g of AR $ZnSO_4$ $7H_2O$ (M. Wt. 287.54) in distilled water in a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

2) EDTA solution (0.05 M): Dissolve 4.7 g of Na_2H_2 EDTA $2H_2O$ (M. Wt. 372.24) in distilled water In a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

3) pH – 10 Buffer: Mix 57 mL of concentrated ammonia solution with 7 g of ammonium Chloride taken in a 250 ml beaker and transfer the resultant solution quantitatively into a 100 mL volumetric flask, making use of small amounts of distilled water. Finally make up the solution to the mark with distilled water and homogenise.

4) Eriochrome black T (EBT) indicator: Disslove 0.2 g of Eriochrome Black T solid in a mixture of 15 mL of triethanolmaine and 5 mL of ethyl alcohol.

Procedure

PART – A: ***Standardisation of EDTA Solution with Standard Zinc(II) Solution:*** Wash all the glass apparatus first with tap water and then rinse with distilled water. Rinse the burette with EDTA solution and fill it with the same solution up to the zero mark, avoiding air bubbles. Clamp the burette to its stand. Rinse the 20 mL pipette with standard zinc sulphate solution thoroughly and pipette out 20 mL of the same solution into a clean 250 mL conical flask. Add into it 20 mL of distilled water, 1 mL of pH – 10 buffer and 1 – 2 drops of EBT indicator. Titrate the contents of the conical flask with EDTA solution taken in the burette until the colour of the solution in the conical flask changes from ***wine red*** to ***blue***. Repeat the procedure with fresh 20 mL aliquots of zinc(II) solution until two successive concurrent titres are obtained. Enter the data obtained in Table-A and calculate the strength of EDTA as shown under Table-A.

Table-A: Standardisation of EDTA solution using standard zinc(II) solution.

S. No.	Volume of zinc(II) solution pipetted out, mL V_1	Burette readings, mL		Volume of EDTA solution rundown from burette, mL V_2
		Initial	Final	
1 2 3	20.00 20.00 20.00			

CALCULATIONS: As the mole ratio of zinc(II) ion to EDTA is 1:1 in Zn – EDTA complex, the concentration of EDTA can be calculated using the equation,

$V_1 M_1 = V_2 M_2$ where

V_1 = Volume of standard zinc(II) solution pipetted out = 20.00 mL

M_1 = Molarity of standard zinc(II) solution =

V_2 = Volume of EDTA solution rundown form burette = mL and

M_2 = Molarity of EDTA solution

Therefore, the molarity of EDTA solution, M_2 is calculated by substituting the known values of M_1, V_1 and V_2 in the equation,

$$M_2 = V_1 M_1 / V_2 =$$

Concentration of EDTA solution, M_2 = M

PART – B: ***Determination of Zinc(II) Concentration in the Problem Solution:*** Make up the zinc(II) problem solution given in 100 mL flask to the mark with distilled water and homogenise. Rinse the 20 mL pipette with the problem solution of zinc(II) twice and pipette out 20 mL of the same solution into a clean 250 mL conical flask. Add to it 20 mL of distilled water followed by 1 mL of

pH – 10 buffer and 1 – 2 drops of EBT indicator. Titrate the contents of the conical flask with EDTA solution taken in the burette until the colour of the solution in the conical flask changes from ***wine red*** to ***blue***. Repeat the procedure with fresh 20 mL aliquots of the problem solution until two successive concurrent titres are obtained. Enter the relevant data in Table-B and calculate the strength and amount of zinc(II) present in 100 mL as shown under Table-B.

Table – B: Determination of zinc(II) in the given problem solution.

S. No.	Volume of problem solution pipetted out, mL V_3	Burette readings, mL		Volume of EDTA solution rundown from burette, mL V_2^I
		Initial	Final	
1	20.00			
2	20.00			
3	20.00			

CALCULATIONS: Find out the concentration of zinc(II) in the problem solution using the equation,

$$V_3 M_3 = V_2^I M_2 \quad \text{where}$$

V_2^I = Volume of EDTA solution rundown form burette (Part-B) = mL

M_2 = Molarity of EDTA solution (Part – A)

V_3 = Volume of problem solution pipetted out = 20.00 mL and

M_3 = Molarity of zinc(II) in the problem solution

Calculate the concentration of zinc(II) in the problem solution, M_3 by substituting the known values of M_2, V_2^I and V_3 in the equation,

$$M_3 = V_2^I M_2 / V_3$$

The Concentration of zinc(II) in the problem solution, M_3 = M

Amount of zinc(II) in the given problem solution = $\frac{M_3 \text{ x At. Wt. of Zn x } 100}{1000} = M_3 \text{ x } 65.39 / 10$

REPORT: The amount of zinc(II) present in the given problem solution is g.

Roll/Regd. No.	Amount of zinc(II), g		% Error
	Given	Reported	

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8. Determination of Nickel(II) by EDTA Method

Discussion: Even though the formation constant of Nickel – EDTA complex is large, the reaction between nickel(II) and EDTA is relatively slow kinetically at pH – 10 and a direct titration of nickel(II) with EDTA using EBT indicator is not satisfactory. However, when nickel(II) is treated with excess of EDTA (excess compared to what is required stoichiometrically), the reaction goes to completion under the same conditions and nickel(II) can be determined by back titrating the excess EDTA using standard zinc(II) or magnesium(II) solution using EBT as indicator. In this experiment, zinc(II) is suggested for back titrating the excess EDTA solution.

Solutions and Reagents

1. Standard zinc sulphate solution (0.05 M): Dissolve 3.594 g of AR $ZnSO_4$ $7H_2O$ (M. Wt. 287.54) in distilled water in a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise .

2) EDTA solution (0.05 M): Dissolve 4.7 g of Na_2H_2 EDTA $2H_2O$(M. Wt. 372.24) in distilled water in a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise .

3) Nickel (II) solution (0.05M): Dissolve 5.00 g of $(NH_4)_2$ SO_4 $NiSO_4$ $6H_2O$ (M. Wt. 395) in distilled water in a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

4) pH – 10 Buffer: Mix 57 mL of concentrated ammonia solution with 7 g of ammonium Chloride taken in a 250 ml beaker and transfer the resultant solution quantitatively into a 100 mL volumetric flask, making use of small amounts of distilled water. Finally make up the solution to the mark with distilled water and homogenize, taking due care to avoid spilling.

5) Eriochrome black T (EBT) indicator: Disslove 0.2 g of Eriochrome Black T solid in a mixture of 15 mL of triethanolmaine and 5 mL of ethyl alcohol.

Procedure

PART – A: ***Standardisation of EDTA Solution with Standard Zinc(II) Solution:*** Wash all the glass apparatus first with tap water and then rinse with distilled water. Rinse the burette with EDTA solution and fill it with the same solution up to the zero mark, avoiding air bubbles. Clamp the burette to its stand. Rinse the 20 mL pipette with standard zinc sulphate solution thoroughly and pipette out 20 mL of the same solution into a clean 250 mL conical flask. Add into it 20 mL of distilled water, 1 mL of pH – 10 buffer and 1 – 2 drops of EBT indicator. Titrate the contents of the conical flask with EDTA solution taken in the burette until the colour of the solution in the conical flask changes from ***wine red*** to ***blue***. Repeat the procedure with fresh 20 mL aliquots of zinc(II) solution until two successive concurrent titres are obtained. Enter the data obtained in Table-A and calculate the strength of EDTA as shown under Table-A.

Table-A: Standardisation of EDTA solution using standard zinc(II) solution.

S. No.	Volume of zinc(II) solution pipetted out, mL V_1	Burette readings, mL		Volume of EDTA solution rundown from burette, mL V_2
		Initial	Final	
1 2 3	20.00 20.00 20.00			

CALCULATIONS: As the mole ratio of zinc(II) ion to EDTA is 1:1 in Zinc – EDTA complex, the concentration of EDTA can be calculated using the equation,

$V_1 M_1 = V_2 M_2$ where

V_1 = Volume of standard zinc(II) solution pipetted out = 20.00 mL

M_1 = Molarity of standard zinc(II) solution =

V_2 = Volume of EDTA solution rundown form burette = mL and

M_2 = Molarity of EDTA solution

Therefore, the molarity of EDTA solution, M_2 is calculated by substituting the known values of M_1, V_1 and V_2 in the equation,

$M_2 = V_1 M_1 / V_2$ =

Concentration of EDTA solution, M_2 =

PART – B: ***Determination of Nickel(II) Concentration in the Problem Solution:*** Make up the nicklel(II) problem solution, given in 100 mL flask, to the mark with distilled water and homogenize. Rinse the 20 mL pipette thrice with the problem solution of nickel(II) and pipette out 20 mL of the same solution into a clean 250 mL conical flask. Add to it exactly 40.00 mL of M_2 molar EDTA, 20 mL of distilled water followed by 2 mL of pH – 10 buffer and 1 – 2 drops of EBT indicator. Titrate the contents of the conical flask with EDTA solution taken in the burette until the colour of the solution in the conical flask changes from ***blue*** to ***bluish violet***. Repeat the same procedure with fresh 20 mL aliquots of the problem solution until two successive concurrent titres are obtained. Enter the relevant data in Table-B and calculate the strength and amount of zinc(II) present in 100 mL as shown under Table-B.

Table – B: Determination of nickel(II) in the given problem solution.

S. No.	Volume of nickel(II) solution pipetted out, mL V_3	Burette readings, mL		Volume of zinc(II) solution rundown from burette, mL V_2^I
		Initial	Final	
1	20.00			
2	20.00			
3	20.00			

CALCULATIONS: Calculate the excess volume of EDTA added to the problem solution using the equation, $V_4 M_2 = V_2^I M_1$ where

M_1 = Molarity of zinc(II) in the standard solution

V_2^I = Volume of standard zinc(II) solution rundown form burette (Part-B) = mL

V_4 = Volume of EDTA solution added in excess = mL and

M_2 = Molarity of EDTA solution (Part – A)

Calculate the excess volume of EDTA added to Ni(II), V_4 by substituting the known values of M_1, V_2^I and M_2 in the equation,

$$V_4 = V_2^I M_1 / M_2 = Y \text{ mL}$$

Volume of M_2 molar EDTA added to 20.00 mL nickel(II) solution in each case = 40.00 mL

Therefore, volume of EDTA consumed by 20.00 mL of Ni(II) solution = (40.00 - Y) = Z mL

Calculate the Concentration of Ni(II), M_3 in the problem solution using the formula,

$$M_3 = \frac{Z \times M_2}{20} = \quad M$$

The amount of nickel(II) in the given problem solution = $\frac{M_3 \times (\text{At. Wt. of Ni}) \times 100}{1000}$

$$= \frac{M_3 \times 58.69}{10} \quad g$$

REPORT: The amount of nickel(II) present in the given problem solution is g.

Roll/Regd. No.	Amount of nickel(II), g		% Error
	Given	Reported	

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9. Determination of Calcium and Magnesium in a Mixture - EDTA Method

Discussion: Patton and Reeder's Reagent (HHSNNA) permits complexometric determination of calcium in presence of magnesium. This method is useful in the determination of hardness of water and in the analysis of limestone and dolomite. The indicator undergoes a sharp colour change from ***wine red*** to ***pure blue*** at the end point when calcium in solution is titrated with standard EDTA solution at a pH between 12 and 14. Direct titration of a solution containing calcium and magnesium with the standard EDTA solution at a pH of 10 using Eriochrome Black T (EBT) indicator gives the total concentration of calcium and magnesium. As the former titration gives the concentration of calcium only and the later that of the total of calcium and magnesium, it is possible to calculate the concentration of magnesium by difference.

The usefulness of the HHSNNA Reagent for the titration of calcium depends upon the fact that the pH of the solution is sufficiently high to ensure the quantitative precipitation of magnesium as magnesium hydroxide and that calcium forms a more stable complex with the EDTA than does magnesium. At pH - 12, the EDTA does not react with magnesium, present as $Mg(OH)_2$, until all the free calcium and calcium-indicator complex have been complexed by the EDTA.

Solutions and Reagents

1) Standard zinc(II) solution (0.02 M): Dissolve 1.4377 g of AR grade $ZnSO_4$ $7H_20$ (M. Wt. 287.54) in distilled water in a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

2) EDTA solution (0.02 M): Dissolve 1.861 g of Na_2H_2 EDTA $2H_2O$ (M. Wt. 372.24) in distilled water in a 250 mL volumetric flask and finally make up the solution to the mark with distilled water and homogenise.

3) Standard calcium(II) stock solution (0.1 M): Dissolve 1.000 g of AR $CaCO_3$ (M. Wt. 100) in the minimum quantity of dilute hydrochloric acid in a 100 mL volumetric flask, make up to the mark with distilled water and homogenise.

4) Standard magnesium(II) stock solution (0.1 M): Dissolve 2.465 g of AR $MgSO_4$ $7H_2O$ (M. Wt. 246.48) in distilled water in a 100 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

5) Working (Problem) solution of calcium(II) and magnesium(II) [0.01 M each in Ca(II) and Mg(II)]: Making use of a burette, transfer exactly 25 mL each of solutions 3 and 4 (standard stock solutions of calcium and magnesium) in to a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

6) pH – 10 Buffer: Mix 57 mL of concentrated ammonia solution with 7 g of ammonium Chloride taken in a 250 ml beaker and transfer the resultant solution quantitatively into a 100 mL volumetric flask, making use of small amounts of distilled water. Finally make up the solution to the mark with distilled water and homogenize, taking due care to avoid spilling of the solution.

7) Potassium hydroxide solution (4 N): Dissolve 22 g of KOH in 100 mL of distilled water.

8) Eriochrome black T (EBT) indicator: Disslove 0.2 g of Eriochrome Black T solid in a mixture of 15 mL of triethanolmaine and 5 mL of ethyl alcohol.

9) Patton and Reeder's Reagent (HHSNNA)***:*** Grind well 0.2 g of the dye with 20 g of anhydrous sodium sulphate in a mortar.

Procedure

PART – A: ***Standardisation of EDTA Solution with Standard Zinc(II) Solution:*** Wash all the glass apparatus first with tap water and then rinse with distilled water. Rinse the burette with EDTA solution and fill it with the same solution up to the zero mark, avoiding air bubbles. Clamp the burette to its stand. Rinse the 20 mL pipette thoroughly with standard zinc sulphate solution and pipette out 20 mL of the same solution into a clean 250 mL conical flask. Add into it 20 mL of distilled water, 1 mL of pH – 10 buffer and 1 – 2 drops of EBT indicator. Titrate the contents of the conical flask with EDTA solution taken in the burette until the colour of the solution in the conical flask changes from ***wine red*** to ***blue***. Repeat the procedure with fresh 20 mL aliquots of zinc(II) solution until two successive concurrent titres are obtained. Enter the data obtained in Table-A and calculate the strength of EDTA as shown under Table-A.

Table-A: Standardisation of EDTA solution with standard zinc(II) solution.

S. No.	Volume of zinc(II) solution pipetted out, mL V_1	Burette readings, mL		Volume of EDTA solution rundown from burette, mL V_2
		Initial	Final	
1 2 3	20.00 20.00 20.00			

CALCULATIONS: As the mole ratio of zinc(II) ion to EDTA is 1:1 in Zn – EDTA complex, the concentration of EDTA can be calculated using the equation,

$V1\ M_1 = V_2 M_2$ where

V_1 = Volume of standard zinc(II) solution pipetted out = 20.00 mL

M_1 = Molarity of standard zinc(II) solution =

V_2 = Volume of EDTA solution rundown form burette = mL and

M_2 = Molarity of EDTA solution

Therefore, the molarity of EDTA solution, M_2 is calculated by substituting the known values of M_1, V_1 and V_2 in the equation, $M_2 = V_1 M_1 / V_2$ =

Concentration of EDTA solution, M_2 = M

PART – B: ***Determination of Total Concentration of Calcium(II) and Magnesium(II) in the Problem Solution:*** Rinse the 20 mL pipette thrice with the problem solution of calcium and magnesium and pipette out 20 mL of the same solution into a clean 250 mL conical flask. Add to it 20 mL of distilled water followed by 1 mL of pH – 10 buffer and 1 – 2 drops of EBT indicator. Titrate the contents of the conical flask with EDTA solution taken in the burette until the colour of the solution in the conical flask changes from ***wine red*** to ***blue***. Repeat the procedure with fresh 20 mL aliquots of the problem solution until two successive concurrent titres are obtained. Enter the relevant data in Table-B and calculate the total strength of calcium and magnesium as shown under Table-B.

Table – B: Determination of total concentration of calcium and magnesium

S. No.	Volume of problem solution pipetted out, mL V_3	Burette readings, mL		Volume of EDTA solution rundown from burette, mL V_4
		Initial	Final	
1.	20.00			
2.	20.00			
3.	20.00			

CALCULATIONS: Calculate the total concentration of calcium and magnesium in the problem solution using the equation,

$V_3 M_3 = V_4 M_2$ where

M_2 = Molarity of EDTA solution (Part –A)

V_3 = Volume of problem solution pipetted out = 20.00 mL

M_3 = Total molarity of calcium and magnesium in the problem solution and

V_4 = Volume of EDTA solution rundown form burette (Part-B) = mL

Calculate the total concentration of calcium(II) and magnesium(II) in the problem solution, M_3 by substituting the known values of M_2, V_4 and V_3 in the equation, $M_3 = V_4 M_2 / V_3$

Total Concentration of calcium(II) and magnesium(II) in the problem solution, M_3 = M

PART – C: ***Selective Determination of Calcium(II) in the Problem Solution:*** Pipette out 20 mL of the problem solution containing calcium(II) and magnesium(II) into a clean 250 mL conical flask and add 20 mL of distilled water followed by 5 mL of 4N potassium hydroxide and mix the contents of the conical flask thoroughly. Wait for ***three*** minutes with occasional mixing of the contents of the conical flask. Add a pinch of Patton and Reeder's Reagent into the conical flask, mix well and titrate the contents of the conical flask with EDTA solution taken in the burette until the colour of the solution in the flask changes to ***pure blue***. Repeat the procedure with fresh 20 mL aliquots of the problem solution until two successive concurrent titres are obtained. Enter the data obtained in this part in Table-C and calculate the concentrations and amounts of calcium and magnesium as shown under Table-C.

Table –C: Selective determination of of calcium in the mixture of calcium and magnesium.

S. No.	Volume of problem solution pipetted down, mL V_3	Burette readings, mL		Volume of EDTA solution rundown from burette, mL V_5
		Initial	Final	
1.	20.00			
2.	20.00			

CALCULATIONS: The standard EDTA titres obtained with the EBT and Patton and Reeder's indicators form the basis for the evaluation of Ca(II) and Mg(II) concentrations; the former pertains to the total concentration of calcium(II) and magnesium(II) while the later to that of calcium(II) only. Calculate the concentration of calcium only by using the equation,

$V_3 M_4 = V_5 M_2$ where

V_3 = Volume of problem solution pipetted out = 20.00 mL

M_4 = Molarity of calcium only in the problem solution

V_5 = Volume of EDTA solution rundown form burette (Part-C) = mL and

M_2 = Molarity of EDTA solution (Part – A) =

Therefore, the concentration of calcium(II), M_4 in the problem solution is obtained by substituting the known values of M_2, V_5 and V_3 in the equation, $M_4 = V_5 M_2 / V_3$

The concentration of calcium(II) in the problem solution, M_4 = M

I. Amount of calcium(II) in 250 mL of the problem solution = $\frac{M_4 \times (\text{At. Wt. of Ca}) \times 250}{1000}$

$= \frac{M_4 \times 40.08}{4} = 10.02 \times M_4$ g

II. Amount of magnesium(II) in 250 mL of the problem solution

$= \frac{(M_3 - M_4) \times (\text{At. Wt. of Mg}) \times 250}{1000}$

$= \frac{(M_3 - M_4) \times 24.31}{4} = 6.08 \times (M_3 - M_4)$ g

REPORT: Amounts of Ca(II) and Mg(II) present in the given problem solution

Roll/Regd. No.	Amount of Ca(II), g		Amount of Mg(II), g		% Error	
	Given	Reported	Given	Reported	Ca(II)	Mg(II)

Precautions: 1. Patton and Reeder's Reagent should be added only after adding potassium hydroxide solution and waiting for five minutes with occasional mixing – otherwise, a satisfactory end point is not obtained; magnesium(II) forms a lake with the indicator and as the pH of the medium increases the magnesium – indicator lake is precipitated along with the magnesium hydroxide.

2. Addition of excess of indicators is to be avoided as it obscures the colour Transition of the indicator at the end point.

3. Titrations in Part – C have to be carried out slowly and with thorough mixing of the analyte in the conical flask as the material in it is heterogeneous.

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10. Determination of Iron(III) by Photochemical Reduction Method

Discussion: Chemical reactions in which light provides the necessary activation energy for the reaction to take place are known as photochemical reactions. Green plants carry out photosynthesis, a biochemical assimilatory process, by making use of the photochemical reactions. Certain degradative chemical reactions are also brought about by light and such photochemical reactions are now being tried in toxic waste decomposition. Attempts were also made to utilize photochemical reactions in analytical chemistry and the present experiment is an example for it.

Iron(III) forms a yellow compound with oxalate ions which undergoes chemical decomposition in the presence of bright sun light to yield ferrous oxalate.

$$Fe_2(C_2O_4)_3^{3+} \xrightarrow{h\nu} 2\,Fe\,C_2O_4^{2+} + 2CO_2\uparrow$$

Any oxidant which can selectively oxidize iron(II) formed in the above photochemical reduction, without interference from oxalate ions is useful to determine iron(II) in the solution. Sodium vanadate is one such oxidant which suits the situation.

In aqueous medium, vanadium exists in V, IV, III and II oxidation states. The stabilities of these oxidation states depend upon the conditions of the medium. The standard redox potential of V^{V}/V^{IV} system is 1.05 V. Vanadium(V) is quite stable in neutral and weakly acidic solutions and is almost colourless. It gets reduced to vanadium(IV) state by reductants such as iron(II), SO_2, etc., in acid medium. One of the advantages of vanadium(V) as an oxidant is that it does not give rise to induced reactions. This stands in contrast to the oxidations with potassium dichromate and potassium permanganate, which give rise to induced reactions. Further, vanadium(V) does not oxidize oxalate ions under certain experimental conditions.

In general, because of the limited solubility of ammonium vanadate in water, the more readily soluble sodium vanadate is preferred as the oxidant. Thus, sodium vanadate, is a viable oxidant in the present experiment.

Sodium vanadate solution is obtained by treating ammonium vanadate taken in water with a slight excess of sodium carbonate and boiling the resultant solution until the ammonia is expelled completely.

$$2\,NH_4VO_3 + Na_2CO_3 \xrightarrow{\text{Heat}} 2NaVO_3 + 2NH_3\uparrow + H_2O + CO_2\uparrow$$

$$\underset{\text{Sodium meatvanadate}}{NaVO_3} + Na_2CO_3 \longrightarrow \underset{\text{Sodium orthovanadate}}{Na_3VO_4} + CO_2\uparrow$$

Solutions and Reagents

1. ***Standard potassium dichromate solution (0.05 N):*** Dissolve 1.226 g of AR grade potassium dichromate $K_2Cr_2O_7$ (Eq. Wt. 49.04) in distilled water in a 500 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

2. ***Iron(II) solution (0.05 N):*** Weigh about 5 g of ammonium ferrous sulphate hexahydrate, $(NH_4)_2\ Fe(SO_4)_2\ 6H_2O$ (Eq. Wt. 392.16) into a clean 400 mL beaker and dissolve it in a Mixture of 150 mL of water and 50 mL of 5N sulphuric acid. Transfer the solution into a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

3. ***Sodium vanadate solution (0.05 N):*** Weigh 1.5 g of ammonium metavanadate and 1.6 g Of sodium carbonate into a 400 mL beaker and add 250 mL of distilled water to it. Heat The mixture to boiling and continue the boiling until all the ammonia is expelled, as noticed by its smell. Cool the solution to room temperature and filter it into a 250 mL volumetric flask. Dilute the solution to the mark with distilled water and homogenise. .

4. ***Iron(III) solution (0.05 N):*** Weigh out 6.1 g of ammonium ferric sulphate dodecahydrate, $NH_4\ Fe(SO_4)_2\ 12H_2O$ (Eq. Wt. 482.25) into a clean 400 mL beaker and dissolve it in a mixture of 150 mL of water and 10 mL of 5N sulphuric acid. Transfer the solution into a 250 mL volumetric flask, add 40 mL of 5 N sulphuric acid, make up the solution up to the mark with distilled water and homogenise the solution.

5. ***Oxalic acid solution (0.2 N):*** Dissolve 3.15 g of AR $H_2C_2O_4\ 2H_2O$ (Eq. Wt. 63.04) in distilled Water in a 250 mL volumetric flask, make up to the mark with distilled water and homogenise.

6. ***Dilute sulphuric acid solution (5 N):*** Carefully add, in small portions, 70 mL of AR concentrated sulphuric acid to 400 mL of distilled water taken in a 1000 mL beaker. Allow the hot solution to cool to room temperature, make up the volume to 500 mL with distilled water and homogenise.

7. ***Syrupy phosphoric acid (H_3PO_4) (85 %):*** Use the acid strait away***.***

8. ***Diphenylamine (DPA) Indicator:*** Dissolve 1 g of the substance in 100 mL of concentrated sulphuric acid taken in a 250 mL beaker. Finally transfer the liquid into a properly labeled reagent bottle.

PROCEDURE

PART – A: Standardisation of Iron(II) Solution Using Standard Potassium Dichromate Solution: Wash all the glass apparatus first with tap water and then rinse with distilled water. Rinse the burette with the standard potassium dichromate solution and fill it with the same solution up to the zero mark without any air bubbles and clamp the burette to its

stand. Rinse the 20 mL pipette with iron(II)) solution and pipette out 20 mL of the same solution into a clean 250 mL conical flask. To this add 10 mL of distilled water, 15 mL of 5N sulphuric acid and 3 mL of syrupy phosphoric acid followed by 2 drops DPA indicator. Titrate the colourless solution in the conical flask against standard potassium dichromate solution until the colour of the solution changes from green to gray green. Then add the standard potassium dichromate solution slowly, in drops, until the first tinge of blue violet which remains permanent on shaking appears. Note down the burette readings to the nearest 0.05 mL and record them in Table–A. Repeat the titrations with 20 mL aliquots of iron(II) solution until two successive concurrent titers are obtained and enter the readings in the same table. Calculate the concentration of iron(II) as shown under Table-A.

Table - A: Standardisation of iron(II) using standard potassium dichromate solution

S. No.	Volume of iron(II) solution pipetted out, mL V_2	Burette readings, mL		Volume of potassium dichromate solution rundown from burette, mL V_1
		Initial	Final	
1.	20.00			
2.	20.00			
3.	20.00			

CALCULATIONS: Calculate the concentration of iron(II) using the equation,

$$N_1V_1 = N_2V_2 \quad \text{where}$$

N_1 = Normality of the standard potassium dichromate solution =
V_1 = Volume of the standard potassium dichromate solution rundown from burette = mL
V_2 = Volume of iron(II) solution pipetted out = 20.00 mL and
N_2 = Normality of iron(II) solution, which can be calculated as, $N_2 = N_1V_1 / V_2$ =

Therefore, Normality of iron(II) solution N_2 = N

PART – B: Standardisation of Sodium Vanadate Solution with Standard Iron(II) Solution.
Clean the burette first with tap water and then with distilled water. Next, rinse the burette with sodium vanadate solution and fill it with the same solution up to the zero mark without any air bubbles and clamp the burette to its stand. Pipette out 20 mL of iron(II)) solution into a clean 250 mL conical flask. To this add 10 mL of distilled water, 15 mL of 5N sulphuric acid and 3 mL of syrupy phosphoric acid followed by 2 drops DPA indicator. Titrate the colourless solution in the conical flask against sodium vanadate solution taken in the burette until the colour of the solution changes from blue to blue violet; carry out the titration slowly and drop-wise near the end point. Note down the burette readings to the nearest 0.05 mL and record them in Table - B. Repeat the titrations with 20 mL aliquots of iron(II) solution until two successive concurrent titers are obtained and enter the readings in the same table. Calculate the concentration of sodium vanadate as shown under Table - B.

Table - B: Standardisation of sodium vanadate solution using standard iron(II) solution

S. No.	Volume of iron(II) solution pipette out, mL V_2	Burette readings, mL		Volume of vanadate solution rundown from burette, mL V_3
		Initial	Final	
1. 2. 3.	20.00 20.00 20.00			

CALCULATIONS: Calculate the concentration of iron(II) in the solution using the equation,

$N_3 V_3 = N_2 V_2$ where

V_2 = Volume of iron(II) solution pipetted out = 20.00 mL and
N_2 = Normality of iron(II) solution (Part – A) =
N_3 = Normality of sodium vanadate solution = and
V_3 = Volume of sodium vanadate solution rundown from burette = mL

As V_2, N_2 and V_3 are known, calculate the normality of vanadate solution as

$N_3 = N_2 V_2 / V_3 =$

Therefore, Normality of sodium vanadate solution N_3 = N

PART – C: Determination of Iron(III) in the Solution by Photochemical Reduction Method.
Rinse the 20 mL pipette with ***iron(III)*** solution thrice and pipette out 20 mL of the same solution into a clean 250 mL conical flask. To this add 20 mL of N/5 N oxalic acid, 40 mL of 5N sulphuric acid, 20 mL of distilled water and mix well to homogenize. Expose the contents of the conical flask to bright sunlight until the solution becomes completely colourless. Add 3 mL of syrupy phosphoric acid followed by 2 drops DPA indicator into the conical flask and titrate the colourless solution against standard sodium vanadate solution taken in the burette until the colour of the solution changes to gray green. Note down the burette readings to the nearest 0.05 mL and record them in Table - C. Repeat the entire process with 20 mL aliquots of ***iron(III)*** solution until two successive concurrent titers are obtained and enter the readings in the same table.

Table - C : Determination of iron(III) in the solution by photochemical reduction.

S. No.	Volume of ***iron(III)*** solution pipetted out, mL V_4	Burette readings, mL		Volume of vanadate solution rundown from burette, mL V_3^I
		Initial	Final	
1. 2. 3.	20.00 20.00 20.00			

CALCULATIONS: Assuming that all the iron(III) pipetted out is quantitatively reduced to iron(II) by the photochemical reduction process, calculate the concentration of iron(III) using the equation,

$$N_3 V_3^{I} = N_4 V_4 \text{ where}$$

N_3 = Normality of sodium vanadate solution (Part – B) =
V_3^{I} = Volume of sodium vanadate solution rundown from burette (Part – C) = mL
V_4 = Volume of ***iron(III)*** solution pipetted out = 20.00 mL and
N_4 = Normality of **iron(III)** in the problem solution.

Calculate the concentration of iron(III) in the problem solution as N_3, V_3^{I}, and V_4 are known.

Normality of **iron(III)** in the problem solution, $N_4 = N_3 V_3^{I} / V_4$ =

Using N_4, calculate the amount of ***iron(III)*** in the prepared solution as

$$\frac{N_4 \times (\text{At. Wt. of iron}) \times 250}{1000} = \frac{N_4 \times 55.85}{4}$$

REPORT: The amount of iron(III) present in the problem solution is g/250 mL.

Roll/Regd. No.	Amount of ***iron(III)***, g		% Error
	Weighed	Determined	

Precautions: 1. The overall sulphuric acid concentration during the photochemical reduction process should be around 2 N to get reproducible results; higher sulphuric acid concentrations are noticed to lower the rate of photochemical reaction

2. The iron(III) solution should be exposed to bright sun light for sufficient time to achieve quantitative photochemical reduction.

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11. Determination of Chloride by Mohr's Method

Discussion: This is a precipitation titration. In this method, chloride in neutral or faintly alkaline solution is determined by titrating it with a standard solution of silver nitrate using potassium chromate as internal indicator. The pH of the sample must be in the range of 7 – 8, the reasons being: 1) Ag(I) gets precipitated as AgOH at pH greater than 8 and 2) CrO_4^{2-} transforms into $Cr_2O_7^{2-}$ at pH less than 7.

$$Ag^+ + OH^- \xrightarrow{\text{pH > 8}} AgOH\downarrow$$

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2\,HCrO_4^{1-} \leftrightarrow 2\,CrO_4^{2-} + 2\,H^+$$

< 7 pH > 8

At lower pH, $HCrO_4^{1-}$ being a weak acid, CrO_4^{2-} ion concentration decreases requiring higher concentration of Ag(I) ions for the solubility product of Ag_2CrO_4 to be exceeded thus leading to higher results. However, in many cases, the required pH can easily be maintained by adding a pinch of pure $CaCO_3$. In practice, neutral solution of chloride taken in the conical flask is directly titrated with standard silver nitrate solution taken in the burette using potassium chromate solution as internal indicator. As the titration is continued, silver ions combine with both chloride and chromate ions forming the respective precipitates of silver chloride and silver chromate.

$$Ag^+ + Cl^- \leftrightarrow AgCl\downarrow \quad (K_{sp} = 1.8 \times 10^{-10})$$

White precipitate

$$2\,Ag^+ + CrO_4^{2-} \leftrightarrow Ag_2CrO_4\downarrow \quad (K_{sp} = 1.1 \times 10^{-12})$$

Reddish brown precipitate

But, the red colour formed due to Ag_2CrO_4 by the addition of each drop of Ag^+ disappears because of the large concentration of Cl^- ions in the solution

$$Ag_2CrO_4 + 2\,Cl^- \leftrightarrow 2\,AgCl\downarrow + CrO_4^{2-}$$

Reddish brown precipitate ***White precipitate***

During the course of the titration as the concentration of Cl^- ions decreases, the red colour disappears more slowly and when all the chloride has been precipitated, a faint reddish or pinkish tinge persists in the solution even after brisk shaking.

Solutions and Reagents

1. ***Standard potassium chloride solution (0.05 N):*** Dissolve 0.932 g of AR grade KCl (Eq. Wt. 74.55) in distilled water in a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

2. ***Silver nitrate solution (0.05 N):*** Dissolve 2.12 g of $AgNO_3$ (Eq. Wt. 169.87) in 250 mL of distilled water in an amber colured bottle and homogenise.

3. Potassium chromate indicator (5% solution): Dissolve 5 g of AR grade potassium chromate in 100 mL of distilled water in a reagent bottle.

4. Calcium carbonate: Use AR grade $CaCO_3$ powder.

PROCEDURE

PART – A: Standardisation of Silver Nitrate Solution. Wash all the glass apparatus first with tap water and then rinse thoroughly with distilled water. Rinse the burette with silver nitrate solution and fill it with the same solution up to the zero mark without any air bubbles and clamp the burette to its stand. Rinse the 20 mL pipette with standard chloride solution and pipette out 20 mL of the same solution into a clean 250 mL conical flask and add 1 mL of potassium chromate indicator. Titrate the contents of the conical flask against silver nitrate solution taken in the burette slowly and with constant swirling of the conical flask until the red colour formed by the addition of each drop disappears more slowly - this is an indication that most of the chloride has been precipitated. Continue the dropwise addition of silver nitrate until a faint but distinct change in colour occurs. This *faint* reddish brown colour should persist even after brisk swirling. Note down the burette readings to the nearest 0.05 mL and record them in Table–A. Repeat the titrations with 20 mL aliquots of standard chloride solution until two successive concurrent titers are obtained and enter the readings in the same table. Calculate the concentration of silver nitrate as shown under Table-A.

Table - A: Standardisation of silver nitrate solution using standard potassium chloride solution.

S. No.	Volume of potassium chloride solution pipetted, mL V_1	Burette readings mL		Volume of silver nitrate solution rundown from burette, mL V_2
		Initial	Final	
1.	20.00			
2.	20.00			
3.	20.00			

CALCULATIONS: Calculate the concentration of silver nitrate solution using the equation,

$N_1V_1 = N_2V_2$ where

N_1 = Normality of the standard potassium chloride solution =
V_1 = Volume of standard potassium chloride solution pipetted out = 20.00 mL
V_2 = Volume of silver nitrate solution rundown from burette = mL and
N_2 = Normality of silver nitrate solution which can be calculated as

$N_2 = N_1V_1 / V_2$ =

Therefore, Normality of silver nitrate solution N_2 = N

PART – B: ***Determination of Chloride Concentration in the Problem Solution:*** Make up the chloride problem solution given in 100 mL flask to the mark with distilled water and homogenize. Rinse the 20 mL pipette twice with the problem solution and pipette out

20 mL of the same solution into a clean 250 mL conical flask. Add 1 mL of potassium chromate indicator and titrate the problem solution against silver nitrate solution taken in the burette as per the procdure described in Part – A above. Note down the burette readings to the nearest 0.05 mL and record them in Table - B. Repeat the titrations with 20 mL aliquots of problem chloride solution until two successive concurrent titers are obtained and enter the readings in the same table. Calculate the concentration of silver nitrate as shown under Table - B.

Table - B: Determination of chloride in the problem solution using silver nitrate solution.

S. No.	Volume of problem chloride solution pipetted out, mL V_3	Burette readings, mL		Volume of silver nitrate solution rundown from burette, mL V_2^{I}
		Initial	Final	
1.	20.00			
2.	20.00			
3.	20.00			

CALCULATIONS: Calculate the concentration of chloride in the problem solution using the equation,

$$N_2 V_2^{I} = N_3 V_3 \quad \text{where}$$

V_2^{I} = Volume of silver nitrate solution rundown from burette (Part – B) = mL and
N_2 = Normality of silver nitrate solution (calculated in Part – A) =
N_3 = Normality of chloride in the problem solution = and
V_3 = Volume of problem chloride solution pipetted out = 20.00 mL

As N_2, V_2^{I} and V_3 are known, calculate the concentration of chloride in the problem solution, N_3.

$$N_3 = N_2 V_2^{I} / V_3 = \quad N$$

The amount of chloride in the problem solution $= \frac{N_3 \times (\text{eq. Wt. of } Cl^-) \times 100}{1000} = \frac{N_3 \times 35.45}{10}$

$$= 3.545 \times N_3 \quad g$$

REPORT: The amount of chloride present in the problem solution = g

Roll/Regd. No.	Amount of chloride, g		% Error
	Weighed	Determined	

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12. Titrimetric Determination of Calcium by Permanganate Method

Discussion: Calcium forms a sparingly soluble oxalate, CaC_2O_4 in weakly acidic or neutral solutions which is readily soluble in dilute sulphuric acid liberating free oxalic acid. Hence, the calcium may be determined indirectly by dissolving the washed CaC_2O_4 precipitate in dilute sulphuric acid and titrating the liberated oxalic acid with a standard oxidant solution like that of potassium permanganate. The permanganametric method is widely used for the determination of calcium in materials like dolomite. In practice, the calcium is precipitated as the oxalate by the addition of ammonium oxalate solution to a dilute hydrochloric acid solution of calcium followed by neutralization of the acid with dilute ammonia solution. The washed precipitate is dissolved in dilute sulphuric acid solution and the liberated oxalic acid titrated with standard potassium permanganate solution.

$$CaCl_2 + (NH_4)_2C_2O_4 \longrightarrow CaC_2O_4\downarrow + 2\,NH_4Cl$$

$$CaC_2O_4\downarrow + H_2SO_4 \longrightarrow CaSO_4 + H_2C_2O_4$$

$$5\,H_2C_2O_4 + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 10CO_2\uparrow + 8H_2O$$

From the above discussion, one can conclude that the amount of calcium present in an aliquot of the calcium solution is equivalent to that of calcium oxalate precipitated from the aliquot which in turn is equivalent to that of the oxalic acid set free from calcium oxalate precipitate, by the addition of dilute sulphuric acid.

Solutions and Reagents

1. ***Calcium(II) solution (0.10)N:*** Weigh accurately 1.25 g of AR grade $CaCO_3$ into a clean 250 mL volumetric flask, dissolve it in the minimum quantity of dilute hydrochloric acid, make up the solution to the mark with distilled water and homogenise.

2. ***Standard oxalic acid solution (0.10 N):*** Dissolve 1.575 g of AR $H_2C_2O_4\,2H_2O$ (Eq. Wt. 63.04) in distilled water in a 250 mL volumetric flask, make up the solution to the mark with distilled water and homogenise.

3. ***Potassium permanganate solution (0.1 N):*** Dissolve 0.8 g of $KMnO_4$ solid (Eq. Wt. 31.6) in *260 mL* distilled water in a 400 mL beaker and heat to boiling. Cool the solution to room temperature, filter through glass wool into an amber coloured bottle and preserve it.

4. ***Ammonium oxalate solution (6 %):*** dissolve 6 g of AR grade ammonium oxalate in 100 mL of distilled water and homogenise the solution.

5. ***1:1 Hydrochloric acid***

6. ***1:1 ammonium hydroxide solution.***

7. Methyl red indicator: Dissolve 100 mg of the substance in 100 mL of distilled water.

8. Dilute sulphuric acid solution (5 N): Carefully add, in small portions, 70 mL of AR grade concentrated sulphuric acid to 400 mL of distilled water taken in a 1000 mL beaker. Allow the hot solution to cool to room temperature, make up the volume to 500 mL with distilled water and homogenise.

PROCEDURE

As potassium permanganate is not a primary standard substance, first of all its solution has to be standardized before proceeding to the determination of calcium in the problem solution.

PART – A: ***Standardisation of Permanganate Solution Using Standard Oxalic Acid Solution.*** Wash all the glass apparatus first with tap water and then rinse with distilled water. Rinse the burette with $KMnO_4$ solution and fill it with the same solution up to the zero mark, avoiding air bubbles. Clamp the burette to its stand. Rinse the 20 mL pipette with standard oxalic acid solution and pipette out 20 mL of the same solution into a clean 250 mL conical flask. To this add 20 mL each of 5N sulphuric acid and 10 ml distilled water. Heat the contents of the conical flask to a temperature of about 70 – 80 ^{o}C (appearance of first few bubbles in the solution). Stop the heating and titrate the contents of the conical flask in the hot condition against potassium permanganate solution taken in the burette until the colour of the solution in the conical flask changes from colourless to permanent pale pink ***(Note: Initially, the reaction is very slow and hence the next drop of permanganate is to be added only after the colour due to the earlier drop is completely discharged).*** Note down the burette readings to the nearest 0.05 mL and record them in Table – A. Repeat the above process, each time pipetting 20 mL aliquots of standard oxalic acid solution, until two successive concurrent titers are obtained. Enter the data in Table-A and calculate the concentration of permanganate solution, as shown under Table-A.

Table-A: Standardisation of potassium permanganate solution using standard oxalic acid solution

S. No.	Volume of oxalic acid solution pipetted out, mL V_1	Burette readings, mL		Volume of permanganate solution rundown from burette, mL V_2
		Initial	Final	
1.	20.00			
2.	20.00			
3.	20.00			

CALCULATIONS: Calculate the concentration of permanganate solution using the equation, $N_1V_1 = N_2V_2$ where,

N_1 = Normality of standard oxalic acid solution =

V_1 = Volume of oxalic acid solution pipetted out = 20.00 mL

V_2 = Volume of permanganate solution rundown from burette = mL and

N_2 = Normality of permanganate solution

As N_1 , V_1 and V_2 are known, calculate the normality of permanganate soution, N_2 as

$$N_2 = \frac{N_1V_1}{V_2} =$$

Normality of $KMnO_4$ solution N_2 =

PART – B: ***Determination of Calcium Using Standard Potassium Permanganate Solution.***

Pipette down 20 mL of the calcium(II) problem solution into each of the two 400 mL beakers provided with glass stirring rods. To each of the beakers add 5 mL of concentrated hydrochloric acid followed by 2 drops of methyl red indicator and dilute the solution to 200 mL with distilled water. Adopt the following procedure with respect to each of the two samples.

Heat the solution in the beaker to boiling and add to it 25 mL of 6 % aqueous solution of ammonium oxalate taken in a burette, very slowly and with constant stirring with the glass rod. Add to the resultant hot solution 1:1 ammonia solution taken in a burette dropwise and with constant stirring until the mixture turns colourless or pale yellow. Allow the solution containing the precipitate to stand without any further heating for at least one hour. Test the supernatant solution for completeness of precipitation of calcium using a few drops of ammonium oxalate solution. If no precipitate is formed now, proceed as mentioned below.

Decant the clear supernatant solution into another beaker through an ashless filter paper (Whatman No. 40 or 540) fitted in a funnel, collect the filtrate and test with a few drops of precipitating reagent; if a precipitate forms, the entire precipitate has to be discarded and the procedure repeated with a fresh 20 mL aliquot of the problem solution. If no precipitate forms from the filtrate, discard the filtrate, transfer the precipitate in the first beaker on to the filter paper fixed in the funnel with the aid of a jet of hot distilled water from the wash bottle. Use rubber tipped (‘policeman’) glass rod to remove any precipitate adhering to the walls of the beaker or to the stirring rod, and transfer the precipitate to the filter paper. Wash the precipitate with small portions of cold distilled water. Let each portion of the wash solution to drain through the filter before adding the next. Continue the washing until the filtrate from the last wash solution is free from chloride and oxalate. Remove the funnel from the beaker containing the washings

Keep the stem of the funnel inside a clean 500 mL conical flask and pierce a hole at the vertex of the filter paper cone making use of a pointed glass rod and wash the bulk of the precipitate through the funnel into the conical flask with hot distilled water. Treat the filter paper in the funnel with small quantities of dilute sulphuric acid repeatedly and again wash into the flask. Finally, wash the filter paper thoroughly with hot distilled water and collect the washing into the same conical flask; no trace of calcium be left out either in the filter paper or in the funnel. Adjust the total volume of the solution to about 200 mL after adding enough dilute sulphuric acid into the conical flask such that the overall sulphuric acid concentration lies between 1.5 to 2 N.

Heat the contents of the conical flask to a temperature of about 70 – 80 ^{o}C (appearance of first few bubbles in the solution). Stop the heating and titrate the contents of the conical flask in the hot condition against potassium permanganate solution taken in the burette until the colour of the solution in the conical flask changes from colourless to permanent pale pink. Note down the burette readings to the nearest 0.05 mL and record them in Table – B. Enter the results obtained with the second aliquot also in Table–B and calculate the concentration and amount of calcium(II) in the sample solution as shown under Table – B.

Table-B: Determination of calcium(II) using standard potassium permanganate solution

S. No.	Volume of calcium(II) solution pipetted out, mL V_3	Burette readings, mL		Vol. of permanganate solution rundown from burette, mL V_2^{I}
		Initial	Final	
1. 2.	20.00 20.00			

CALCULATIONS: Calculate the concentration of calcium(II) in the sample solution using the equation $N_2V_2^{1} = N_3V_3$ where

N_2 = Normality potassium permanganate solution (Part – A) =

V_2^{I} = Volume potassium permanganate solution rundown from burette in Part – B = mL

V_3 = Volume of calcium(II) sample solution pipetted out = 20.00 mL and

N_3 = Normality of calcium(II) in sample solution.

Therefore, $N_3 = \frac{N_2 V_2^{I}}{V_3}$ = N

Calculate the amount of calcium(II) present in 250 ml as

$$\frac{N_3 \times (\text{Eq. Wt. of Ca(II)}) \times 250}{1000} = \frac{N_3 \times 20.04}{4} = 5.01 \times N_3 = \quad g$$

REPORT: Amount of iron(II) present in the given 100 ml sample solution _____ g

Roll/Regd. Number	Amount of iron(II), g		% Error
	Given	Reported	
	1) 2)		

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III. GRAVIMETRIC ANALYSIS

1. Gravimetric Determination of Barium as Barium Sulphate

Discussion: Barium(II) in very dilute hydrochloric acid medium can be quantitatively precipitated as sparingly soluble barium sulphate in the presence of a slight excess concentration of sulphate and weighed as $BaSO_4$ after heating to a temperature of 900 – 1000 ^{0}C. This is the basis for the gravimetric determination of barium as barium sulphate and this method of determination of barium is widely employed. The solubility of barium sulphate in cold water is about 2.5 mg L^{-1}; however, it is greater in hot water or in dilute hydrochloric or nitric acid and less in solutions containing common ion.

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2\,HCl$$

Barium sulphate may also be precipitated from solution using Sulphamic acid solution which produces sulphate ions on boiling (Homogeneous precipitation method).

$$\underset{\text{Sulphamic acid}}{NH_2SO_3H} + H_2O \longrightarrow NH_4^+ + SO_4^{2-} + H^+$$

The former method is described below.

Solutions and Reagents

1. Barium chloride solution: Dissolve 1.30 g of AR grade barium chloride dihydrate, $BaCl_2\ 2H_2O$ in distilled water in a 100 mL volumetric flask, make up to the mark with distilled water and homogenise. Treat this solution or the one given by your instructor as the problem solution.

2. Precipitating reagent - 0.1 M sulphuric acid: Dilute 4.0 mL of 5 N sulphuric acid to 100 mL in a clean glass reagent bottle and homogenise.

3. Concentrated hydrochloric acid.

PROCEDURE

Always remember that any gravimetric procedure has to be carried out taking at least ***two*** identical aliquots of the problem solution.

Pipette down 20 mL of the barium salt solution into a 400 mL beaker provided with a glass stirring rod, add 1.0 mL of concentrated hydrochloric acid and dilute the solution to 160 mL with distilled water. Heat the solution to boiling and add to it 15 mL of 0.1 M sulphuric acid solution taken in a burette, slowly and with constant stirring with the glass rod. Allow the precipitate to settle for two minutes and test the supernatant liquid for complete precipitation by adding a few drops of 0.1 M sulphuric acid. If a precipitate forms, add slowly a further 3 mL of 0.1 M H_2SO_4 solution, allow the precipitate to settle as before

and test again; repeat this operation until an excess of sulphuric acid is present. When an excess of the precipitating reagent has been added, cover the beaker with a watch glass, keep the solution hot but not boiling for an hour in order to allow for complete precipitation.

Decant the clear supernatant solution into another beaker through an ashless filter paper (Whatman No. 40) fitted in a funnel, collect the filtrate and test it with a few drops of precipitating reagent; if a precipitate forms, the entire sample has to be discarded and the procedure repeated with a fresh 20 mL aliquot of the problem solution. If no precipitate forms, discard the filtrate and transfer the precipitate in the first beaker on to the ashless filter paper fixed in the funnel with the aid of a jet of hot distilled water from the wash bottle. Use rubber tipped ('policeman') glass rod to remove any precipitate adhering to the walls of the beaker or to the stirring rod and transfer the precipitate to the filter paper. Wash the precipitate with small portions of distilled water. Direct the jet as near the top of the filter paper as possible and let each portion of the wash solution to drain through the filter paper before adding the next. Continue the washing until 5 mL of the wash solution gives no opalescence with one or two mL of silver nitrate solution acidified with dilute nitric acid solution; eight to ten washings are usually required.

Fold the moist filter paper around the precipitate and place it in a silica crucible, previously ignited to redness, cooled in desiccator and weighed. Dry the paper by placing the loosely covered crucible upon a clay pipe triangle, several centimeters above a small flame. Then gradually increase the heat until the filter paper chars and volatile matter is expelled - do not allow the paper to burst into flame. When the charring is complete, raise the temperature of the crucible to dull redness and burn of the carbon with free access of air. When the precipitate is white, ignite the crucible at red heat (900 – 1000 ^{0}C) for 10 – 15 minutes. Then allow the crucible to cool somewhat in air, transfer it to the desiccator and when cold, weigh the crucible with lid along with its contents. Repeat the process of ignition for 10-minute periods, subsequent cooling in desiccators, etc., until a constant weight ($\pm$ 0. 0002 g) is attained.

CALCULATIONS: Calculate the amount of barium present in the sample solution as follows:

Weight of the empty crucible with lid after ignition, W_1 = g
Weight of $BaSO_4$ and the crucible with lid after ignition, W_2 = g
Weight of $BaSO_4$ obtained from 20.00 mL of the problem solution, ($W_2 - W_1$) = W g

In one molecule of $BaSO_4$ there is one ion of Ba. In other words, 233.4 g of $BaSO_4$ contains 137.33 g of barium.

Hence, W g of barium sulphate is equivalent to $\frac{137.33 \times W}{233.4}$ gram of barium =

As this much of barium is present in 20 mL aliquot, amount of barium in the given sample solution is equal to

$$\frac{137.33 \times W \times 100}{233.4 \times 20} = \quad g$$

Substitute the numerical value of W in the above equation, calculate the amount of barium in the sample solution and report your result.

Report: Amount of barium present in the sample solution = g.

Roll/Regd. No.	Amount of barium, g		% Error
	Weighed	Determined	
	1) 2)		

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2. Gravimetric Determination of Sulphate as Barium Sulphate

Discussion: The method described for the determination of barium can also be extended for the gravimetric determination of sulphate, with certain necessary modifications in the procedure. The method consists in slowly adding a dilute solution of barium chloride to a hot solution of sulphate, slightly acidified with hydrochloric acid.

$$K_2SO_4 + BaCl_2 \longrightarrow BaSO_4 \downarrow + 2KCl$$

The precipitate is filtered off, washed with water, carefully ignited at a temperature of 900 – 1000 ^{0}C and finally weighed as $BaSO_4$. The modified procedure as applicable to the determination of sulphate is described below.

Solutions and Reagents

1. Barium chloride solution (0.2 M): Dissolve 5 g of AR grade barium chloride dihydrate, $BaCl_2\ 2H_2O$ in 100 mL distilled water.

2. Potassium sulphate solution (0.1 M): Weigh accurately 1.743 g of AR grade potassium sulphate into a clean 100 mL volumetric flask, dissolve and make up to the mark with distilled water. Homogenise the solution.

3. Concentrated hydrochloric acid

PROCEDURE

Pipette down 20 mL of the potassium sulphate solution into a 400 mL beaker provided with a glass stirring rod, add 1.0 mL of concentrated hydrochloric acid and dilute the solution to 200 mL with distilled water. Heat the solution to boiling and add to it 15 mL of 0.2 M barium chloride solution taken in a burette, slowly and with constant stirring with the glass rod. Allow the precipitate to settle for two minutes and test the supernatant liquid for complete precipitation by adding a few drops of 0.2 M barium chloride solution. If a precipitate forms, add slowly a further 3 mL of 0.2 M barium chloride solution, allow the precipitate to settle as before and test again; repeat this operation until an excess of barium chloride is present. When an excess of the precipitating reagent has been added, cover the beaker with a watch glass, keep the solution hot but not boiling for an hour in order to allow for complete precipitation.

Decant the clear supernatant solution into another beaker through an ashless filter paper (Whatman No. 40) fitted in a funnel, collect the filtrate and test it with a few drops of precipitating reagent; if a precipitate forms, the entire sample has to be discarded and the procedure repeated with a fresh 20 mL aliquot of the analyte solution. If no precipitate forms, discard the filtrate and transfer the precipitate in the first beaker on to the ashless filter paper fixed in the funnel with the aid of a jet of hot distilled water from the wash

bottle. Use rubber tipped glass rod to remove any precipitate adhering to the walls of the beaker or to the stirring rod and transfer the precipitate to the filter paper. Wash the precipitate with small portions of distilled water. Direct the jet as near the top of the filter paper as possible and let each portion of the wash solution to drain through the filter paper before adding the next. Continue the washing until 5 mL of the wash solution gives no opalescence with one or two mL of silver nitrate solution acidified with dilute nitric acid solution; eight to ten washings are usually required. Fold the moist filter paper around the precipitate and place it in a silica crucible, previously ignited to redness, cooled in desiccator and weighed. Dry the paper by placing the loosely covered crucible upon a clay pipe triangle, several centimeters above a small flame. Then gradually increase the heat until the filter paper chars and volatile matter is expelled - do not allow the paper to burst into flame. When the charring is complete, raise the temperature of the crucible to dull redness and burn of the carbon with free access of air. When the precipitate is white, ignite the crucible at red heat (900 – 1000 ^{0}C) for 10 – 15 minutes. Then allow the crucible to cool somewhat in air, transfer it to the desiccator and when cold, weigh the crucible with lid along with its contents. Repeat the process of ignition for 10-minute periods, subsequent cooling in desiccators, etc., until a constant weight ($\pm$ 0. 0002 g) is attained.

CALCULATIONS: Calculate the amount of sulphate present in the sample solution as follows:

Weight of the empty crucible with its lid after ignition, W_1 = g
Weight of $BaSO_4$ and the crucible with its lid after ignition, W_2 = g
Weight of $BaSO_4$ obtained from 20.00 mL of the problem solution, $(W_2 - W_1) = W$ g

In one molecule of $BaSO_4$ there is one ion of SO_4^{2-}. In other words, 233.4 g of $BaSO_4$ contains 96.06 g of sulphate.

Hence, W g of barium sulphate is equivalent to $\frac{96.06 \times W}{233.4}$ gram of sulphate =

As this much of sulphate is present in 20 mL aliquot, amount of sulphate in the given sample solution is equal to

$$\frac{96.06}{233.4} \times \frac{W \times 100}{20} = \quad g$$

Substitute the numerical value of W in the above equation and report your result.

Report: Amount of sulphate present in the sample solution = g.

Roll/Regd. No.	Amount of sulphate, g		% Error
	Weighed	Determined	
	1) 2)		

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3. Gravimetric Determination of Calcium as Calcium Carbonate

Discussion: Calcium(II) in weakly acidic solution is precipitated as calcium oxalate monohydrate, $CaC_2O_4\ H_2O$ by treating a hot solution of calcium(II) with ammonium oxalate solution and neutralizing the acidity with ammonium hydroxide solution.

$$Ca^{2+} + C_2O_4^{2-} + H_2O \longrightarrow CaC_2O_4\,H_2O\downarrow$$

The precipitate is washed with dilute ammonium oxalate solution and ultimately weighed as $CaCO_3$ after heating it at 475 – 525 ^{0}C in an electrical muffle furnace. Calcium carbonate, $CaCO_3$ is the most satisfactory form of calcium for the gravimetric determination of calcium , since unlike CaO and CaC_2O_4, $CaCO_3$ is stable and non-hygroscopic.

$$CaC_2O_4 \xrightarrow{\textbf{475 – 525 }^0\textbf{C}} CaCO_3 + CO\uparrow$$

The solubility of calcium oxalate monohydrate in water is 0.0067 and 0.0140 g at 25 ^{0}C and 95 ^{0}C respectively. Owing to the common ion effect, the solubility of $CaC_2O_4H_2O$ is less in neutral solutions containing moderate concentrations of ammonium oxalate. Therefore, a dilute solution of ammonium oxalate is preferred as the wash liquid to wash the precipitated calcium oxalate.

Solutions and Reagents

1***. Calcium(II) solution (0.25 M):*** Weigh accurately 2.5 g of AR grade $CaCO_3$ into a clean 100 mL volumetric flask, dissolve it in the minimum quantity of dilute hydrochloric acid, make up the solution to the mark with distilled water and homogenise.

2. Ammonium oxalate solution (4 %): dissolve 6 g of AR grade ammonium oxalate in 150 mL of distilled water and homogenise the solution.

3. 1:1 Hydrochloric acid

4. 1:1 Ammonium hydroxide solution

5. Methyl red indicator: Dissolve 100 mg of the substance in 100 mL of distilled water.

PROCEDURE

Pipette down 20 mL of the calcium(II) sample solution into a 400 mL beaker provided with a glass stirring rod, add 5 mL of concentrated hydrochloric acid followed by 2 drops of methyl red indicator and dilute the solution to 200 mL with distilled water. Heat the solution to boiling and add to it 50 mL of 4 % aqueous solution of ammonium oxalate taken

in a burette, very slowly and with constant stirring with the glass rod. Add to the resultant solution 1:1 ammonia solution taken in a burette dropwise and with constant stirring until the mixture turns colourless or light yellow in colour. Allow the solution containing the precipitate to stand without any further heating for at least one hour. Test the supernatant solution for complete precipitation of calcium, using a few drops of ammonium oxalate solution. If no precipitate is formed now, proceed as mentioned below.

Decant the clear supernatant liquid through a preheated and weighed silica ***Gooch*** crucible. Transfer the precipitate quantitatively to the crucible with jets of distilled water from wash bottle and wash it with a cold solution (0.1 %) of ammonium oxalate repeatedly until the washings are chloride free. Dry the precipitate in the crucible at 100^0 C in an air oven for one hour and then transfer the crucible along with the dried precipitate to a muffle furnace maintained at 500^0 C. Continue the heating at 500 ^{0}C for two hours such that the complete decomposition of calcium oxalate to calcium carbonate takes place. Cool the crucible with its contents first in air, for a while, then in a desiccator and finally weigh it. Repeat the process of heating the crucible containing $CaCO_3$ at 500^0 C in muffle furnace and weighing it after cooling in a desiccator until a constant weight ($\pm$ 0. 0002 g) is attained.

CALCULATIONS: Calculate the amount of calcium present in the sample solution as follows:
Weight of the empty crucible after heating in muffle furnace W_1 = g
Weight of $CaCO_3$ and the crucible after heating in muffle furnace W_2 = g
Weight of $CaCO_3$ obtained from 20.00 mL of the problem solution, ($W_2 - W_1$) = W g

In one molecule of $CaCO_3$ there is one Ca^{2+} ion. In other words, 100.1 g of $CaCO_3$ contains 40.08 g of calcium.

Hence, W g of $CaCO_3$ is equivalent to $\frac{40.08 \times W}{100.1}$ gram of calcium. As this much of calcium is present in 20 mL aliquot, amount of calcium in the given sample solution is equal to

$$\frac{40.08 \times W \times 100}{100.1 \times 20} = \quad g$$

Substitute the numerical value of W in the above equation and report your result.

Report: Amount of calcium present in the sample solution = g.

Roll/Regd. No.	Amount of calcium, g		% Error
	Weighed	Determined	
	1)		
	2)		

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