MANIPAL INSTITUTE
OF TECHNOLOGY
MANIPAL
(A constituent unit of MAHE, Manipal)

DEPARTMENT OF CHEMISTRY

CERTIFICATE

This is to certify that Ms./Mr. ……..

Reg. No.……..…….Section: …… Roll No: …….

has satisfactorily completed the course of experiments in **Engineering Chemistry Laboratory [CHM 1061]** prescribed by the Manipal Academy of Higher Education for First Year B.Tech. Degree course in the Chemistry Laboratory at MIT, Manipal, in the academic year 20 -20 .

Date: …….....

Signature
Faculty in Charge

Signature
Head of the Department

CONTENTS

Course learning outcomes

At the end of the laboratory course, students will be able to;

- Demonstrate analytical and technical skills to work effectively and safely in a chemical laboratory environment.
- Perform volumetric analysis of water, ore and pigment.
- Explain conductometric, potentiometric titrations with an understanding of the theory.
- Formulate meaningful conclusions by interpreting laboratory data.

General scheme of evaluation

- **In-semester assessments (60%)**

Continuous evaluation = 10/lab session **60**

- **End-semester examination (40%)**
  - Written examination: Duration:1/2 h, **15**
  - Performance of experiment:

    Duration: 1.5 h **25**

Instructions to the students

❖ General instructions:

- ✓ Cultivate the habit of coming well-in-time to laboratory classes along with the necessary stationary items.
- ✓ Maintain pin-drop silence during the demonstration and practical session.
- ✓ Take an active interest in laboratory activities and give meticulous attention to detail.
- ✓ Take questions/comments with an open mind and participate in discussions.
- ✓ Train yourself to contribute to improving academic performance. Use a positive mental attitude.
- ✓ Invest time and energy to read the laboratory manual and related books. Follow the recommended procedures in the laboratory manual.
- ✓ Practice producing a better-written answer in the language of a particularsubject.
- ✓ Compete with a concentrated, planned & systematic way. Have faith in your ability to deal with situations.
- ✓ Inform the instructor immediately in the event of an injury. Inform the laboratory staff at the counter about any damages/breakages of the equipment/glassware.
- ✓ Show the readings and calculations in the practical manual book to the teacher concerned and get their signature.
- ✓ If you miss any practical class because of medical reasons or representing the institute in any event then you may be permitted to perform those experiments during the repetition laboratory class.

❖ **Safety instructions:**

- ✓ Eating, drinking or smoking in the laboratory is strictly prohibited.
- ✓ Do not use a beaker or water from the laboratory taps for drinking purposes.
- ✓ Locate the nearest first aid box and become familiar with its contents and their proper use.
- ✓ Keep your hands away from your mouth, nose, eyes, and face while working.
- ✓ Always wash with abundant water any part of your body that comes into contact with any chemical.
- ✓ Be cautious at all times when handling chemicals, especially those about which you know little.
- ✓ Read reagent bottle labels carefully before using the contents and watch out for any warning labels.
- ✓ Never look directly into the mouth of a test tube or flask containing a reaction mixture.
- ✓ Avoid mixing or heating chemicals close to your face to avoid splashing droplets of reaction mixture.
- ✓ Avoid skin contact with laboratory chemicals due to absorption of some chemicals through the skin. Ensure that open cuts or scratches on the body donot come in contact with any chemicals.
- ✓ Wash your hands thoroughly with soapy water at the end of the laboratory period.

Experiment No.: 1 **Date:**

ALKALIMETRIC TITRATION

Aim of the experiment:

To estimate the amount of oxalic acid crystals dissolved per litre of the given solution using approximately decinormal sodium hydroxide solution and pure crystals of oxalic acid

Background information:

Volumetric analysis is a quantitative chemical analysis method that is used to determine the volume of a solution of accurately known concentration (standard solution) which is required to react quantitatively with a measured volume of a solution of unknown concentration. The process of determination of volume of standard solution required to react completely with a solution of the substance to be determined is called as titration. The solution of known concentration is called the titrant and the solution of known volume but unknown concentration is called the analyte. The equivalence point is the point in a titration where stoichiometrically equivalent amounts of analyte and titrant are present whereas the end point is the point at which an observable physical change like color signals the equivalence point. The advantages of such an analysis include high precision, require simpler apparatus and can be quickly performed. A visual indicator is a compound that exhibits colors depending on the pH of its surroundings. There are four types of titrations based on the reactions employed in volumetric analysis; i) acid-base titrations ii) redox titrations iii) precipitation titrations and iv) complexometric titrations. Alkalimetry, to determine the strength of unknown alkaline solution, is a simple experiment that is useful and informative in demonstrating the basic principles of titrations. The importance of such simple experiments cannot be overestimated, as they directly represent the identity and image of a quantitative analysis and serve as evidence of scientific value facilitating the technical skill up-gradation. The experiment represents the learning by measuring volume of a solution, through experimentation andexhibits apparently strong links to the remaining laboratory experiments. Theconcentration of the analyte is determined from the stoichiometry of the reaction and thevolume of the titrant required to carrying it out. The particular purpose of this experiment is to estimate the amount of oxalic acid dissolved per litre of the solution using acid-base titrations.

Principle and outline:

Oxalic acid reacts with sodium hydroxide according to the following equation.

$$2\ NaOH + H_2C_2O_4 \longrightarrow Na_2C_2O_4 + 2H_2O$$

One molecule of oxalic acid = 2 molecules of NaOH

= 2 equivalents of NaOH

Equivalent weight of oxalic acid crystals $[H_2C_2O_4\ 2H_2O]$ = $\frac{\text{Molecular weight}}{2} = \frac{126}{2} = 63$

A standard solution of oxalic acid is prepared by dissolving a known weight of it in a known volume of water. Then the given sodium hydroxide solution is standardized by titrating a known volume of this standard oxalic acid solution against sodium hydroxide solution taken in the burette. Acid-base indicators are usually effective over a range of several pH units. It is essential for accurate determinations that the color change is sharp at the equivalence point with addition of a drop of titrant. Since oxalic acid is a weak acid and sodium hydroxide is a strong base, phenolphthalein is used as the indicator (pHrange: 8.3-10). The above titration is repeated with the given oxalic acid solution.

Procedure:

(i) Preparation of standard oxalic acid solution:

Weigh out accurately about 1.5 g of pure oxalic acid crystals into a 250 mL standard flask. Dissolve it in a small amount of distilled water. Make up to the mark with distilled water. Shake well for uniform concentration.

***(ii) Standardization of sodium hydroxide solution*:**

Pipette out 25 mL of prepared oxalic acid solution into a clean conical flask. Add 3 drops of phenolphthalein indicator to it. Fill a clean burette with the given sodium hydroxide solution after washing with water and rinsing with a small amount of sodium hydroxide solution. Note the initial burette reading. Titrate the solution in the conical flask against sodium hydroxide solution in the burette carefully in the beginning and drop-wise towards the end of the titration shaking the solution all the while. Appearanceof a permanent pale pink color marks the end point. Note the final burette reading. Repeat the titration to get concordant values.

iii) Estimation of oxalic acid in the given solution:

Repeat the above titration with the given oxalic acid solution instead of the prepared standard oxalic acid solution. Obtain the concordant values.

Result:

The weight of oxalic crystals dissolved per litre of the solution =_____g

Observation and calculations:

i) Preparation of standard oxalic acid solution:

Weight of the weighing bottle + oxalic crystals, W_1 =_____g
Weight of the bottle after transferring the crystals, W_2 =_____g
Weight of oxalic acid crystals taken, $W = (W_1 - W_2)$ =_____g

Strength of the oxalic acid (OA) solution prepared, $N_{OA} = \frac{W \times 4}{\text{Equivalent weight}}$

$= \frac{\times 4}{63}$

=_____N

ii) Standardization of sodium hydroxide solution:

Solution taken in the burette = Given NaOH solution

Solution taken in the conical flask = 25 mL of prepared oxalic acid solution
Indicator used = 3 drops of phenolphthalein
Color change = Colorless to pale pink

Trials →	**1**	**2**	**3**
Final burette reading			
Initial burette reading			
Volume of NaOH added (mL)			

Agreeing value, V_{NaOH} =_____mL

25 mL of_____N oxalic acid solution = V_{NaOH} mL of NaOH solution.

Strength of the given NaOH solution $N_{NaOH} = \frac{V_{OA}\, N_{OA}}{V_{NaOH}} = \frac{25\, N_{OA}}{V_{NaOH}}$

=

=_____N

iii) Estimation of oxalic acid:

Solution taken in the burette = Given NaOH solution

Solution taken in the flask = 25 mL of given oxalic acid solution
Indicator used = 3 drops of phenolphthalein
Color change = Colorless to pale pink

Trials →	**1**	**2**	**3**
Final burette reading			
Initial burette reading			
Volume of NaOH added (mL)			

Agreeing value, V_{NaOH} =_____mL
25 mL of the given oxalic acid solution = V_{NaOH} mL of NaOH solution.
Strength of the given oxalic acid solution, $N_{OA} = \frac{V_{NaOH}\, N_{NaOH}}{V_{OA}} = \frac{V_{NaOH}\, N_{NaOH}}{25}$

=

=_____N

Weight of oxalic acid crystals present per litre of the solution = Normality **X** Equivalent weight

= $N_{OA} \times 63$
=
= g

Review Questions:

1. Define the normality of a solution. What is a buffer solution?
2. Distinguish between the equivalence point and the end point of a titration.
3. What is an indicator? Give an example of acid-base and redox indicators.
4. Provide examples of complexometric and redox titration types
5. Which meniscus would you choose when you fill potassium permanganate and potassium dichromate solutions in a burette? Explain your reasoning.
6. What is titration? Why is it inaccurate to blow the last bit of solution out of a pipet?

Experiment No.: 2 **Date:**

TOTAL HARDNESS OF WATER

Aim of the experiment:

To estimate the total hardness of the given sample of water by EDTA method using approximately 0.02 M EDTA solution and solid calcium carbonate

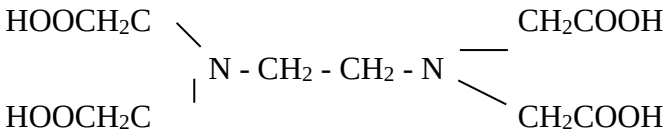
Background information:

Hardness in water is caused by dissolved salts mostly, calcium and magnesium carbonates, bicarbonates or sulfates, but sometimes also those of iron, aluminum and manganese in certain geographical locations. The effectiveness of soap as a cleaning agent is reduced when used in hard water. Hard water consumes a large quantity of soap as it is difficult to produce lather and unsuitable for laundry purposes. The metal ions react with the stearate ions producing an insoluble scum (soap film) before any lather is formed. Soap film tends to remain behind and produces visible deposits on clothing that makes fabrics feel stiff. It also attaches to the insides of bathtubs, sinks and washing machines. Hard water produces scale (insoluble deposit) on the inside surface of the water pipes or tea kettles and industrial scale apparatus like heaters and boilers which is called 'boiler scale'. Water purification and recycling is now a major industry. The hard water scale (ppm) is constructed to consist of six levels of degree of hardness. In the increasing order of degree of hardness these are: very soft (0-70), soft (70-140), slightly hard (140-210), moderately hard (210-320), hard (320-530) and very hard (above 530). If the water tested is very hard on the hardness grade of water, we can safely conclude that it is unfit for drinking purpose and for industrial use. The purpose of the experimentis to determine the total hardness of water quantitatively by titrating a known volume of water sample against standard ethylenediamine tetraacetic acid (EDTA) solution using eriochrome black-T as indicator.

Principle and outline:

Water containing soluble salts (bicarbonates, chlorides and sulphates) of calcium and magnesium (less frequently iron and aluminum) is called hard water. Bicarbonates produce temporary hardness, while chlorides and sulphates produce permanent hardness. Temporary and permanent hardness together are called total harness. Hardness is expressed in parts of $CaCO_3$ equivalents per million parts of water, i.e. ppm or mg of $CaCO_3$ equivalents per litre or dm^3 of water, i.e. mg/L or mg/dm^3.

EDTA is ethylene diammine tetra acetic acid. It has the structural formula shown below;



EDTA, $H_4Y(H_4C_{10}H_{12}O_8N_2)$ is insoluble in water. Its disodium salt, Na_2H_2Y is readily soluble in water. Analar material of the salt is in dihydrate form: $Na_2H_2C_{10}H_{12}O_8N_2.2H_2O$. (Molecular weight = 372.24).

EDTA combines with all metal ions in 1:1 ratio and forms highly soluble complex ions. Thus, when EDTA solution is added to hard water, Ca^{2+} and Mg^{2+} ions combine with EDTA and form highly soluble complex ions, CaY^{2-} and MgY^{2-}, respectively.

$$H_2Y^{2-} + Ca^{2+} \rightarrow CaY^{2-} + 2H^+$$
$$H_2Y^{2-} + Mg^{2+} \rightarrow MgY^{2-} + 2H^+$$

Removal of H^+ ions produced increases the stability of the complex ions formed. This is achieved by maintaining pH of the solution in basic range using an appropriate buffer solution.

Eriochrome black-T (EBT) is a suitable indicator for this titration. It is a triprotic acid: H_3D. It dissociates remarkably easily giving the first H^+ ion and hence exists as H_2D^- in its solutions. Further dissociation of H_2D^- is pH dependent as shown below.

$$H_2D^- \rightarrow H^+ + HD^{2-} \rightarrow H^+ + D^{3-}$$

Red ← Blue ← Yellow- Orange

pH pH

5.3 – 7.3 10.5 - 12.5

It exists as HD^{2-} in the pH range 7-11, exhibiting blue color. Many metal ions like Mg^{2+} & Ca^{2+} form red colored soluble complex ions with HD^{2-}.

$$HD^{2-} + Ca^{2+} \rightarrow CaHD$$

Blue Red

$$HD^{2-} + Mg^{2+} \rightarrow MgHD$$

Blue Red

Hence EBT is known as a metal ion indicator. These complexes are less stable than the EDTA complexes of the corresponding metal ions.

When EBT indicator is added to hard water at pH 10, HD^{2-} of the indicator forms red complex ions with a small fraction of Ca^{2+} and Mg^{2+}, depending upon the quantity of indicator used. When EDTA is added to this solution, it complexes all the free Ca^{2+} and Mg^{2+} ions present. Ca^{2+} and Mg^{2+} ions combined with the indicator start reacting with EDTA, when the solution does not contain free Ca^{2+} & Mg^{2+} ions. When enough EDTA is added to react with all the Ca^{2+} and Mg^{2+} combined with the indicator, free indicator, HD^{2-} ions form in the solution. This happens at the end point and hence color changes from red to blue at this point.

$$CaHD + H_2Y^{2-} \rightarrow CaY^{2-} + HD^{2-} + 2H^+$$
Red Blue

$$MgHD + H_2Y^{2-} \rightarrow MgY^{2-} + HD^{2-} + 2H^+$$
Red Blue

NH_4OH - NH_4Cl buffer is used to maintain the pH at10 during the titration.

A standard solution of $CaCO_3$ is prepared by weighing 0.5 gm of the substance. A known volume of this solution is titrated against the given EDTA solution using Eriochrome black-T indicator. A buffer solution of NH_4Cl-NH_4OH is added to maintain pH value at 10. Thus, EDTA is standardized. The experiment is repeated with water sample. From the titre value molarity of water sample and hence hardness of water are calculated. The molecular weight of $CaCO_3$ is100 g/mL and it is the least soluble salt (solubility in water = 0.0013 g/mL) among other salts present in hard water. The hardness of water is generally expressed as calcium carbonate equivalent.

Procedure:

i) Preparation of standard calcium carbonate solution:

Weigh accurately the calcium carbonate solid given in weighing bottle into a 50 mL beaker. Add dilute HCl is slowly till the solid completely dissolves. Neutralize the solution with NaOH solution till a white precipitate is formed. Dissolve the precipitate in a minimum amount of dilute HCl. Transfer quantitatively to a 250 mL standard flask using a glass rod and a funnel. Make up the solution to the mark with distilled water. Shake well for uniform concentration.

ii) Standardisation of EDTA solution:

Pipette out 25 mL of prepared calcium solution into a clean conical flask. Add 2 mL of NH_4Cl-NH_4OH buffer solution, followed by 3 drops of Eriochrome black-T indicator. The solution turns to wine red color. Titrate this against EDTA solution taken in the burette. The end point is indicated when the solution turns to blue color without reddish tinge. Repeat titration to get concordant values.

iii) Estimation of hardness of water:

Pipette out 25 mL of given hard water into a clean flask. Add 2 mL of NH_4Cl - NH_4OH buffer solution, followed by 3 drops of Eriochrome black-T indicator. The solution turns to wine red color. Titrate this against EDTA solution taken in the burette. The endpoint is indicated when the solution turns to blue color without reddish tinge. Repeat the titration to get agreeing values.

Result:

Total hardness of the given sample of water =_____ ppm $CaCO_3$ or its equivalents.

Observation and calculations:

i) Preparation of standard $CaCO_3$ solution:

Weight of the weighing bottle + $CaCO_3$ powder, W_1 =_____g

Weight of the bottle after transferring the powder, W_2 =_____g

$\therefore$ Weight of $CaCO_3$ dissolved/250 mL solution, $W_1 - W_2 = W$ =_____g

ii) Standardisation of EDTA solution:

Solution taken in the burette = Given EDTA solution

Solution taken in the flask = 25 mL of $CaCO_3$ solution+ 2 mL of NH_4Cl–NH_4OH buffer solution

Indicator used = 3 drops of Eriochrome black T

End point = Change of color from wine red to blue

Trials →	**1**	**2**	**3**
Final burette reading			
Initial burette reading			
Volume of EDTA added (mL)			

Agreeing value, V_1 = mL

iii) Estimation of hardness of water:

Solution taken in the burette = Given EDTA solution

Solution taken in the flask = 25 mL of hard water + 2 mL of NH_4Cl–NH_4OH buffer solution

Indicator used = 3 drops of Eriochrome black-T

End point = Change of color from wine red to blue

Trials →	**1**	**2**	**3**
Final burette reading			
Initial burette reading			
Volume of EDTA added (mL)			

Agreeing value, V_2 = mL

V_1 mL of EDTA solution reacts completely with 25 mL of Ca^{2+} solution

$\therefore$ V_1 mL of EDTA solution $\equiv$ 25 mL of Ca^{2+} solution

$\equiv$ W/10 g of $CaCO_3$

$\therefore$ 1 mL of EDTA solution $\equiv \frac{W}{10} \times \frac{1}{V_1}$ g of $CaCO_3$

V_2 mL of EDTA reacts completely with Ca^{2+} & Mg^{2+} ions present in 25 mL of water sample.

$\therefore$ 25 mL of water sample $\equiv V_2$ mL of EDTA solution

$$[\frac{W}{10} \times \frac{1}{V1}]V2 \text{ g of } CaCO_3$$

= ……..=X g

25 mL or 25 g of water sample contains X g of $CaCO_3$

$\therefore$ 1 million (i.e. 10^6) g of water contains $\rightarrow X \times 10^6$ / 25 g of $CaCO_3$

Hardness of water = $(X \times 10^6) / 25$ ppm or mgms/L of $CaCO_3$ or its equivalent.

= _____ ppm.

Review Questions:

1. Write the structural formula of EDTA.
2. What is the type of indicator used in the determination of hardness of water?
3. Why is NH_4OH-NH_4Cl buffer added in the estimation of hardness of water?
4. How do you express the total hardness of water?
5. Differentiate between temporary and permanent hardness of water.

Experiment No.: 3 **Date:**

ANALYSIS OF COPPER IN BRASS

Aim of the experiment:

To estimate the percentage of copper in the given sample of brass using a solution of sodium thiosulfate of approximately 0.05 N and a solution of potassium dichromate in a 250 mL standard flask which on dilution up to the mark becomes exactly 0.05 N.

Background information:

An alloy is a substance that contains a mixture of elements and has metallic properties. The copper alloys may be produced with a wide range of properties by varying their composition (becomes harder as the % of zinc increases) and by subjecting them to mechanical/ heat treatment processes making them engineering materials next tosteel in importance. Brass is an alloy of copper and zinc and typical composition is Cu/Zn with 55-80 % Cu & 45-20 % Zn and very small amounts of tin, lead and iron.The proportions of zinc and copper can be varied to create a range of brasses with varying properties and generally, they are stronger and more durable than copper. Brass, an example of substitutional alloy, contains about one-third of the host copper metal replaced by zinc atoms of similar size. We can also describe it as solid solution composed of solid solute and solid solvent. Brass is used for applications where low friction is required such as locks, gears, bearings, doorknobs, ammunition, and valves, for plumbing and electrical applications, and in other traditional household products. Itis widely used in pipes and fittings, for it is easy to forge, cast and stamp. It is also extensively used in making musical instruments such as horns and bells for its acoustic properties. The purpose of the present experiment is to determine the percentage of copper present in the given brass sample by iodometric method.

Principle and outline:

Given sodium thiosulfate solution is standardized using the standard $K_2Cr_2O_7$ solution supplied. Acidified $K_2Cr_2O_7$ liberates equivalent quantity of iodine by oxidation when excess KI is added to it.

$$K_2Cr_2O_7 + 8\ HCl \rightarrow 2\ KCl + 2\ CrCl_3 + 4\ H_2O + 3\ (O)$$

$$6\ KI + 6\ HCl + 3\ (O) \rightarrow 6\ KCl + 3\ I_2 + 3\ H_2O$$

Liberated I_2 is titrated with sodium thiosulfate solution using starch solution near the end-point. Color changes from dark blue to bright green. This is due to the presence of $CrCl_3$ in the solution.

Brass is an alloy of copper (55-80 %) and zincs (45-20 %). Weighed quantity of brass is dissolved in concentrated nitric acid. Both copper and zinc dissolve in the acid as their nitrates. Reddish brown nitrogen dioxide gas evolves, when the alloy dissolves.

$$Cu + 4\ HNO_3 \rightarrow Cu(NO_3)_2 + 2\ NO_2 + 2\ H_2O \qquad \textbf{(1)}$$

Cupric nitrate, $Cu(NO_3)_2$ liberates equivalent quantity of iodine by oxidation when excess KI is added to the brass solution.

$$2\ Cu(NO_3)_2 + 4\ KI \rightarrow \underset{\text{Cuprous iodide (white)}}{Cu_2I_2\downarrow} + I_2 + 4\ KNO_3 \qquad \textbf{(2)}$$

Iodine is sparingly soluble in water. It dissolves readily in KI solution forming tri iodide, I_3^- ions. Hence excess KI solution should be added to dissolve liberated iodine. The titration should not be prolonged unnecessarily as iodine vaporizes and escapes from the solution. By estimating the amount of iodine liberated, copper is estimated.

Iodine is estimated by titrating it with a standard sodium thiosulfate, $Na_2S_2O_3$ (hypo), solution.

$$I_2 + 2\ Na_2S_2O_3 \rightarrow \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6} + 2\ NaI \qquad \textbf{(3)}$$

According to the equation **2**,

2 molecules of $Cu(NO_3)_2 \equiv$ 2 atoms of iodine

$\equiv$ 2 equivalents of iodine

$\therefore$ Equivalent weight of copper = its atomic weight = 53.57

The following precautions must be observed in this titration;

(i) Dissolved oxides of nitrogen (NO, NO_2) must be removed from brass solution, before adding KI solution to it. Otherwise, the oxides of nitrogen also liberate I_2 from KI and hence the iodine liberated will be more than the equivalent amount of Cu^{2+} ions present in the solution. By boiling the brass solution with urea, oxides of nitrogen are decomposed & are removed as H_2O and N_2.

$$\underset{\text{Urea}}{(NH_2)_2CO} + NO_2 + NO \rightarrow 2\ N_2 + CO_2 + 2\ H_2O \qquad \textbf{(4)}$$

(ii) Strong mineral acids present in the brass solution must be neutralised with NH_4OH before adding KI to it. If these acids are present in the solution, dissolved oxygen liberates iodine by oxidizing cuprous iodide, Cu_2I_2 to cupric iodide, CuI_2, which is unstable, and changes to Cu_2I_2 and I_2. Hence iodine liberated will be more than the equivalent amount of Cu^{2+} ions present in the solution.

(iii) The brass solution also should not be alkaline before adding KI. Cu^{2+} ions precipitate in alkaline medium as bluish white $Cu(OH)_2$ precipitate, which does not liberate iodine on adding KI. Hence iodine liberated will be less than the equivalent amount of Cu^{2+} ions present in the solution. Thus alkaline solution should be made acidic by adding a weak acid like acetic acid before adding KI solution. Best result will be obtained by maintaining the pH at 4.0 - 5.5.

(iv) Freshly prepared starch solution is used as indicator in this titration. Starch reacts with iodine in the presence of iodide to form intensely blue colored complex. When enough $Na_2S_2O_3$ is added to react with all iodine, including from the starch-iodine complex, the intense blue color will be discharged and the solution becomes colorless. It appears milky white due to the presence of white Cu_2I_2 precipitate at the end-point.

(v) The starch indicator must not be added until just before the end-point is reached. If the starch solution is added when the iodine concentration is high, some iodine may remain adsorbed even at the end-point. Adsorbed I_2 reacts slowly with $Na_2S_2O_3$ solution, resulting in a higher titre value. Hence starch indicator is to be added whenthe solution in the flask is faintly yellow which indicates low concentration of iodine.

Procedure:

(i) Preparation of standard potassium dichromate ($K_2Cr_2O_7$) solution:

Weigh out 0.6 g of $K_2Cr_2O_7$ crystals into a 250 mL standard flask. Dissolve and make up to the mark with distilled water. Shake well for uniform concentration.

(ii) Standardisation of sodium thiosulfate solution:

Pipette out 25 mL of $K_2Cr_2O_7$ solution into a conical flask. Add about 5 mL of (1/3 t.t.) concentrated HCl and 10 mL of 10 percent KI solution. Titrate the liberated iodine against $Na_2S_2O_3$ solution taken in the burette, until the solution is yellowish green in color. Now, add 1 mL of starch solution and continue the titration slowly until the blue color just

disappears. A bright green-colored solution will remain at the end of the titration. Repeat the titration for concordant values.

(iii) Estimation of copper in brass:

Weigh accurately about 1 g of clean and dry brass pieces given in weighing bottle and transfer it to a 250 mL beaker. Add concentrated nitric acid little by little till all the brass pieces are completely dissolved. Take care neither to add any excess of acid nor tolose any part of the solution. Dilute this solution with a little distilled water. Add about1g of urea to the solution and boil till all nitrogen and its oxides are expelled. Cool the solution and transfer quantitatively into a 250 mL standard flask using a funnel and a glass rod. Wash the beaker and glass rods several times with distilled water and transferwashings to the standard flask. Make the solution up to the mark with distilled water. Shake well for uniform concentration. This is called brass solution.

Pipette out 25 mL of brass solution into a conical flask. Add ammonium hydroxide solution drop-wise until a bluish-white precipitate is obtained. Dissolve the precipitate by adding dilute acetic acid and add 10 mL of 10 percent KI to the resulting solution. Titrate the liberated iodine against standardized sodium thiosulfate solution in the burette till the brown solution turns to pale yellow. Add at this stage 1 mL of starch solution when it turns to dark blue color. Continue the addition of thiosulfate till the blue color just disappears. This marks the end point. Repeat the titration to get agreeing values.

Result:

Percentage of copper in brass: _____

Observation and calculations:

(i)Preparation of standard potassium dichromate($K_2Cr_2O_7$) solution:

Weight of the weighing bottle + $K_2Cr_2O_7$ crystals, W_1 = _____g

Weight of the bottle after transferring the crystals, W_2 = _____g

Weight of $K_2Cr_2O_7$ crystals taken, W = ($W_1 - W_2$) = _____g

Strength of the $K_2Cr_2O_7$ solution prepared, $N_{K2Cr2O7} = \frac{W \times 4}{\text{Equivalent weight}}$

$$= \frac{\quad \times 4}{49.03}$$

ii) Standardisation of $Na_2S_2O_3$ solution:

Solution taken in the burette = Given $Na_2S_2O_3$ solution

Solution taken in the flask = 25 mL of $K_2Cr_2O_7$ solution+ 1/3 test tube of conc. HCl + 10 mL of 10 percent KI solution

Indicator used = 1 mL of starch solution

End point = Disappearance of blue color

Trials →	**1**	**2**	**3**
Final burette reading			
Initial burette reading			
Volume of sodium thiosulfate added (mL)			

Agreeing value, V = _____ mL

$\therefore$ Strength of given $Na_2S_2O_3$ solution $= \frac{25 \times N_{K2Cr2O7}}{V_{Thiosulfate}}$

$= \frac{25 \times 0.05}{\quad}$

$=$ _____ N

(iii) Estimation of copper in brass:

Weight of the weighing bottle + brass pieces, W_1 = _____ g

Weight of weighing bottle (empty), W_2 = _____ g

$\therefore$ Weight of brass dissolved/250 mL solution, $(W_1 - W_2)$ = _____ g

Titration of brass solution:

Solution taken in the burette = Given $Na_2S_2O_3$ solution

Solution taken in flask = 25 mL of brass solution + NH_4OH + dilute acetic acid + 10 mL of 10 percent KI solution

Indicator used = 1 mL of starch solution

End point = Disappearance of blue color

Trials →	**1**	**2**	**3**
Final burette reading			
Initial burette reading			
Volume of sodium thiosulfate added (mL)			

Agreeing value, $V_{Na2S2O3}$ = _____ mL

$\therefore$ Strength of copper in brass solution, N_{Cu} $= \frac{V_{Thiosulphate} \times N_{Thiosulphate}}{25}$

$= \frac{\quad \times \quad}{25}$

$= \_\_\_\_\_ N$

$\therefore$ Weight of copper in the whole of 250 mL of the solution $= \frac{N_{Cu} \times 63.57}{4}$

$= \frac{\quad \times 63.57}{4}$

$= \_\_\_\_\_ = X$ g

$\therefore$ Percentage of copper in brass $= \frac{X \times 100}{(W_1 - W_2)}$

$= \frac{\quad \times 100}{\quad}$

=

Review Questions:

1. What is the principle of iodometric titration?
2. Why is urea added in the determination of copper in brass?
3. Why is starch added towards the end in iodometric titrations?
4. What is the function of potassium iodide in the estimation of copper in brass?
5. Write the balanced chemical reaction between brass solution and potassium iodide.

Experiment No.: 4 **Date:**

ANALYSIS OF IRON IN HEMATITE

Aim of the experiment:

To estimate the weight of iron in hematite solution ($FeCl_3$) given in a 250 mL standard flask using approximately deci-normal $K_2Cr_2O_7$ solution and pure crystals of Mohr's salt (internal indicator method)

Background information:

Iron is the most abundant element on Earth as a whole and an important industrial resource. The main ores of iron include hematite (Fe_2O_3), magnetite (Fe_3O_4), pyrite (FeS_2), limonite ($Fe_2O_3.H_2O$) and siderite ($FeCO_3$). The principal ore of iron, hematite, contains mainly Fe_2O_3 and a small amount of silica (SiO_2).The iron ores are primarily used to make stainless steel that are highly corrosion resistant and different types of steels show different properties that find applications in making iron wire, nails, chains, horseshoes, rails, knives, razors, cutting tools and drill bits. The world production of iron ore is about 970 million tons and 5 % is the contribution from India. The estimation of iron is not only very important from the point of view of commercial interest but is also represents an academically significant laboratory lesson for engineering students. The purpose of the current experiment is to determine the percentage of Fe_2O_3 in the given sample of hematite ore.

Principle and outline:

Mohr's salt is a double sulphate, $FeSO_4(NH_4)_2SO_4.6H_2O$. Acidified $K_2Cr_2O_7$ oxidises $FeSO_4$ of Mohr's salt to $Fe_2(SO_4)_3$ as follows;

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

$$6\,FeSO_4 + 3\,H_2SO_4 + 3\,(O) \rightarrow 3\,Fe(SO_4)_3 + 3\,H_2O$$

6 molecules of Mohr's salt = 3 atoms of (O) = 6 equivalents.

$\therefore$ Equivalent weight of Mohr's salt = its molecular weight = 392.

A standard solution (approx. 0.1N) of Mohr's salt must be prepared in a 250 mL standard flask by weighing accurately about 39.2/4 = 9.8 g of the salt. $FeSO_4$ hydrolysesin aqueous solution as:

$$FeSO_4 + 2H_2O \rightarrow Fe(OH)_2\downarrow + H_2SO_4$$
$$\leftarrow$$

Presence of dilute H_2SO_4 will shift the above equilibrium to the left and prevent hydrolysis.

Given $K_2Cr_2O_7$ solution is standardised, using the standard Mohr's salt solution prepared. Diphenylamine is used as internal indicator. Appearance of dark bluish violet color marks the end-point.

Hematite ore is an ore of iron, containing the metal in oxide form, Fe_2O_3 (ferric oxide). When its solution in HCl acid is prepared, the oxide dissolves as ferric chloride, $FeCl_3$. Ferric salts are oxidizing agents and they do not react with another oxidizing agent like, $K_2Cr_2O_7$. $FeCl_3$ must be reduced to ferrous chloride, $FeCl_2$ that is a reducing agent and hence reacts with $K_2Cr_2O_7$, as shown below.

$$K_2Cr_2O_7 + 4\ H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4\ H_2O + 3\ (O) \qquad \textbf{(1)}$$

$$6\ FeCl_2 + 6HCl + 3\ (O) \rightarrow 6\ FeCl_3 + 3H_2O \qquad \textbf{(2)}$$

According to equation 1, 1 molecule of $K_2Cr_2O_7 \equiv 3$ atoms or 6 equivalents of oxygen.

$\therefore$ Equivalent weight of $K_2Cr_2O_7$ = Molecular weight of $K_2Cr_2O_7$ / 6 = 294.18/6
= 49.03

According to equation 2, 6 molecules of $FeCl_2 \equiv 6$ molecules of $FeCl_3$
$\equiv 6$ atoms of iron
$\equiv 3$ atoms or 6 equivalents of oxygen

$\therefore$ Equivalent weight of $FeCl_2$ = Molecular weight of $FeCl_2$ = 126.8
Equivalent weight of $FeCl_3$ = Molecular weight of $FeCl_3$ = 162.2
Equivalent weight of iron = Atomic weight of iron = 55.85

$FeCl_3$ is quantitatively reduced to $FeCl_2$ by adding a slight excess of stannous chloride ($SnCl_2$) solution. Unreacted $SnCl_2$ is destroyed by adding saturated mercuric chloride ($HgCl_2$) solution. Resulting solution containing $FeCl_2$ is titrated with the standardized

solution of $K_2Cr_2O_7$, using diphenylamine as internal indicator.

The precautions given below should be adopted in the experiment:

(i) Only slight excess of $SnCl_2$ should be used to reduce $FeCl_3$ to $FeCl_2$

$$2\ FeCl_3 + SnCl_2 \rightarrow SnCl_4 + 2\ FeCl_2$$

Stannic chloride

$SnCl_2$ solution should be added drop wise to the hot yellow colored solution containing $FeCl_3$ and conccentrated HCl, until the solution becomes colorless and then one or two drops of $SnCl_2$ solution in excess to ensure complete reduction of $FeCl_3$.

(ii) $SnCl_2$ is a strong reducing agent. It reduces $K_2Cr_2O_7$. If the solution is titrated with $K_2Cr_2O_7$ solution, before the destruction of unreacted $SnCl_2$, both $FeCl_2$ and $SnCl_2$ present in the solution react with $K_2Cr_2O_7$, giving rise to higher titre value. Therefore unreacted $SnCl_2$ must be destroyed before titration. It is achieved by adding saturated $HgCl_2$ solution.

$$SnCl_2 + 2\ HgCl_2 \rightarrow Hg_2Cl_2 \downarrow + SnCl_4$$

Mercurous chloride (silky white)

Hg_2Cl_2 does not react with $K_2Cr_2O_7$, even though it is also a reducing agent, since it is present as precipitate and not in solution.

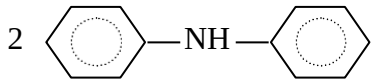
(iii) A silky white precipitate must be produced on adding $HgCl_2$. If the precipitate does not appear, the solution does not contain unreacted $SnCl_2$ and hence reduction of $FeCl_3$ to $FeCl_2$ is incomplete. On the other hand, if a black precipitate of finely divided mercury is produced, the solution contains too much unreacted $SnCl_2$.

$$SnCl_2 + HgCl_2 \rightarrow 2\ Hg \downarrow + SnCl_4$$

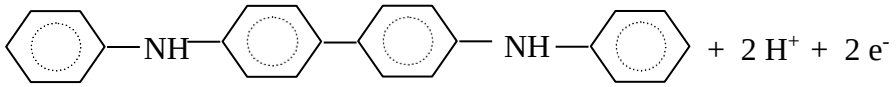
Finely divided mercury (black)

Finely divided mercury, being a good reducing agent reduces $K_2Cr_2O_7$. In either case, the solution must be rejected and the reduction must be repeated with fresh ore solution and a solution containing silky white precipitate should only be used for titration.

Diphenyl amine (I) changes to colorless diphenyl benzidine (II), which is the real indicator and is reversibly oxidized to diphenyl benzidine violet (III)

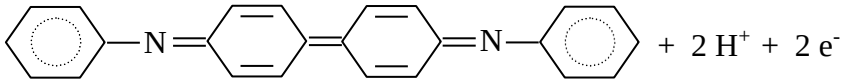


(I) - Colorless



(II) - Colorless

Reduction  Oxidation



(III) - Violet

Formal potential is the potential of the redox system when the ratio of analytical concentrations of reactants and products of half reaction (as they appear in Nernst equation) is unity and concentration of other species in the system are carefully specified. The formal potential of Indicator (III)-Indicator (II) system is around 0.85V. The equivalence potential of $Cr_2O_7^{2-}$ versus Fe (II) is around 1.2. This must be brought close to the formal potential of indicator to have a sharp end-point. Presence ofphosphoric acid (0.5 M H_2SO_4-1 M H_2SO_4) lowers the formal potential of Fe(III)-Fe(II) system to 0.61 V due to complex formation of Fe(III) with phosphate ions, $[Fe(PO_4)_2]^{3-}$.This brings down the equivalence potential to coincide more nearly with the formal potential of indicator. Therefore, H_3PO_4 - H_2SO_4 must be added to the solution to make it 0.5 M in H_3PO_4 and 1 M in H_2SO_4 in this titration using diphenylamine as internal indicator.

Procedure:

(i) Preparation of Mohr's salt solution:

Keep about 10 g Mohr's salt crystals in a weighing bottle. Transfer it into a 250 mL standard flask after weighing accurately. Dissolve the salt is in a little dilute H_2SO_4. Make the solution up to the mark with distilled water and shake well.

(ii) Standardisation of $K_2Cr_2O_7$ solution:

Pipette out 25 mL of the Mohr's salt solution into a conical flask. Add about 8 drops of 1 percent solution of diphenylamine as the indicator. Add about 10 mL of sulphuric acid-phosphoric acid mixture. Titrate the solution slowly with constant stirring against $K_2Cr_2O_7$ solution in the burette. Near the end point the solution becomes bluish violet and remains permanent. This marks the end point. Repeat the titration to get agreeing values.

(iii) Estimation of iron chloride:

Make up the hematite ($FeCl_3$) solution kept in a 250 mL standard flask to the mark with distilled water and shake well. Pipette out 25 mL of this solution is into a conical flask. Add 1/3 test tube of concentrated HCl and heat just to boiling. To the hot solution, drop $SnCl_2$ solution from a burette until the yellow color of the solution just discharges. Add just one or two drops in excess. Cool the hot solution rapidly under the tap to room temperature with protection from the air. Add 5 mL of saturated mercuric chloride solution rapidly in one portion and with thorough mixing. A light silky white precipitate should be obtained. If a black precipitate is obtained or if no precipitate is obtained, it should be rejected and the process must be repeated with another fresh 25 mL portion of the $FeCl_3$ solution. Add about 8 drops of 1 percent solution of diphenylamine as the indicator. Then add about 10 mL of sulphuric acid - phosphoric acid mixture. Titrate this against $K_2Cr_2O_7$ solution in the burette with constant stirring till the solution turns to intense purple or bluish-violet color. This marks the end point. Repeat the titration to get agreeing values.

Result:

Weight of iron dissolved in the whole of the solution kept in a 250 mL standard flask = _____ g.

Observation and calculations:

i) Preparation of standard Mohr's salt solution:

Weight of weighing bottle + Mohr's salt, W_1 = _____ g

Weight of the bottle after transferring, W_2 = _____ g

∴ Weight of Mohr's salt taken, $W = (W_1 - W_2)$ = _____ g

∴ Strength of the solution prepared

$$= \frac{(W_1 - W_2) \times 4}{392}$$

$$= \frac{\times 4}{392}$$

= _____ N

(ii) Standardisation of $K_2Cr_2O_7$ solution:

Solution taken in the burette = Given $K_2Cr_2O_7$ solution

Solution taken in the flask = 25 mL of Mohr's salt solution + 10 mL of H_2SO_4-H_3PO_4 mixture

Indicator used = 8 drops of 1 percent solution of diphenylamine

End point = Appearance of bluish violet color

Trials →	**1**	**2**	**3**
Final burette reading			
Initial burette reading			
Volume of $K_2Cr_2O_7$ added (mL)			

Agreeing value, V_____mL

$\therefore$ Strength of $K_2Cr_2O_7$ solution, $N_{Dichromate}$ = $\frac{25 \times N_{Mohr's\ salt}}{V_{Dichromate}}$

= $\frac{25 \times \quad}{\quad}$

= _____N.

(iii) Estimation of $FeCl_3$:

Solution taken in the burette = Given $K_2Cr_2O_7$ solution

Solution taken in the flask = 25 mL of $FeCl_3$ solution + 1/3 test tube of conc. HCl (Heat to boiling + $SnCl_2$ (cool) + 5 mL of saturated $HgCl_2$ solution + 10 mL of H_2SO_4-H_3PO_4 mixture

Indicator used = 8 drops of 1 percent diphenylamine solution

End point = Appearance of bluish-violet color

Trials →	**1**	**2**	**3**
Final burette reading			
Initial burette reading			
Volume of $K_2Cr_2O_7$ added (mL)			

Agreeing value, V_____mL

$\therefore$ Strength of $FeCl_3$ solution, N_{FeCl3} = $\frac{V_{Dichromate} \times N_{Dichromate}}{25}$

= $\frac{\quad \times \quad}{25}$

= _____ N

$\therefore$ Weight of iron present in the whole of 250 mL = $\frac{N_{FeCl3} \times 55.85}{4}$

= $\frac{\quad \times 55.85}{4}$

= _____ g

Review Questions:

1. What is the main constituent of hematite?
2. What is the function of stannous chloride in the estimation of iron? What will happen if it is added in excess?
3. Why do you add mercuric chloride in the estimation of iron in hematite?
4. Why is the reduction of ferric iron carried out in hot condition?
5. Name the indicator used in the determination of iron in hematite.
6. What is redox reaction? Give an example.

Experiment No.: 5 **Date:**

MANGANESE DIOXIDE IN PYROLUSITE

Aim of the experiment:

To estimate the percentage of MnO_2 in the given sample of pyrolusite, using approximately 1 N oxalic acid solution and a standard potassium permanganate solution of 0.1N

Background information:

Pyrolusite is a principal ore of manganese containing mainly manganese dioxide, MnO_2, and small amounts of silica and iron oxide. Other two less common ores are rhodochrosite ($MnCO_3$) and hausmannite (Mn_3O_4). Pyrolusite is the principal source of manganese, manganese alloys and many manganese compounds like purple $KMnO_4$. It is extensively used in the production of hard steel used for bank vaults, armor plate and rock crushers. The refined electrolytic manganese dioxide (EMD) is used in the manufacture of dry cells. Other industrial applications include its use as an inorganic pigment in ceramics and in glassmaking. It is also used in the brick industry to color bricks red or brown and in the production of potassium permanganate. It is also used as an oxidizing agent (oxidation of allylic alcohols to the corresponding aldehydes or ketones), in organic synthesis (aromatization, oxidative coupling, and thiol oxidation) and as catalyst in the preparation of oxygen from potassium chlorate ($KClO_3$) and in the decomposition of hydrogen peroxide to oxygen and water. The aim of the experiment is to determine the percentage of MnO_2 present in the given pyrolusite sample.

Principle and outline:

Pyrolusite is an ore of manganese-containing the metal as its dioxide, MnO_2. A known weight of pyrolusite is heated with a known excess of oxalic acid solution, in the presence of dilute H_2SO_4. Oxalic acid reduces MnO_2 of the ore to manganese salt. Oxalic acid is oxidized to CO_2 by MnO_2 of the ore.

$$MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O + (O)$$

$$H_2C_2O_4 + (O) \rightarrow H_2O + 2\,CO_2$$

$$MnO_2 + H_2C_2O_4 + H_2SO_4 \rightarrow MnSO_4 + 2\,H_2O + 2\,CO_2\uparrow$$

The unreacted oxalic acid left over is estimated by back titration with standard $KMnO_4$ solution. According to the above equation:

One molecule of MnO_2 $\equiv\equiv$ One atom of oxygen

$\equiv$ Two equivalents of oxygen

$\therefore$ Equivalent weight of MnO_2 $= \frac{\text{Molecular weight}}{2} = \frac{86.94}{2} = 43.47$

Oxalic acid reacts with $KMnO_4$ in the presence of dilute H_2SO_4 as shown in the following equation.

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

$$5\ H_2C_2O_4 + 5\ (O) \rightarrow 5\ H_2O + 10\ CO_2$$

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

A blank titration is conducted by titrating directly the same volume of oxalic acid solution used for the reaction with pyrolusite, against the standard $KMnO_4$ solution.This is called a blank titration. Amount of MnO_2 present in the ore is calculated from the difference between blank and back titre values.Characteristics of titration, of oxalic acid with $KMnO_4$ are given below;

(i) The rate of reaction between $H_2C_2O_4$ and $KMnO_4$ is very slow at room temperature. Hence the oxalic acid solution must be heated to $60^o - 80^o$ C or nearly boiling before titration.

(ii) $KMnO_4$ is a strong oxidizing agent in the presence of a strong mineral acid. So oxalic acid must be acidified with a strong mineral acid like dilute H_2SO_4 before titration. Hydrochloric acid, if used reacts with potassium permanganate giving higher titre values and nitric acid is not suitable for acidification as it is a good oxidizing agent in addition to being an acid.

(iii) Use of an indicator is unnecessary, since as little as 0.01 mL of 0.01 N $KMnO_4$ imparts pale pink color to 100 mL water. Thus, $KMnO_4$ is a self-indicator.

(iv) Manganese ion -Mn^{2+} acts as catalyst for the reaction between $H_2C_2O_4$ and $KMnO_4$. That is why reaction is rapid from the beginning in the back titration, since the solution

contains manganese salt produced from pyrolusite. But in the blank titration, reaction of initial drop of $KMnO_4$ is slow, since the solution does not contain manganese salts. It becomes rapid afterwards, since the solution contains manganese salt produced by the reaction between first few drops of $KMnO_4$ and $H_2C_2O_4$.

Procedure:

(i) Blank titration:

Pipette out 25 mL of given 1 N oxalic acid into a 250 mL standard flask. Make up to the mark with distilled water and shake well. Pipette out 25 mL of this solution is into a conical flask. Add about 2 test tubes of dilute H_2SO_4 and heat to nearly boiling. Titrate the hot solution with the standard $KMnO_4$ solution until permanent pale pink color is produced. Repeat the titration to get agreeing value. Let it be V_1 mL.

(ii) Estimation:

Weigh accurately given pyrolusite ore into a clean conical flask. Pipette out exactly 25 mL of given **1** N oxalic acid into it. Add 50 mL of **4** N H_2SO_4, using a measuring jar. Place a glass funnel on the conical flask and gently boil the contents until all black particles dissolve. Cool the clear solution to room temperature and transfer quantitatively into a 250 mL standard flask. Make up to the mark with distilled water and shake well. Pipette out 25 mL of this solution into a conical flask. Add one test tube of dilute H_2SO_4, heat to gentle boiling. Titrate the hot solution with standard $KMnO_4$ solution until pale pink color is produced. Repeat the titration to obtainagreeing value. Let it be V_2 mL. (V_1-V_2) mL is the volume of standard $KMnO_4$ equivalent to the weight of MnO_2 present in 1/10th of weighed sample of pyrolusite.

Result:

Percentage of MnO_2 in the given sample of pyrolusite = ——————————

Observation and calculations:

(i) Blank titration:

Solution taken in the burette = Standard $KMnO_4$ solution

Solution in the conical flask = 25 mL of made up oxalic acid solution +
2 test tubes dilute H_2SO_4
(heat to gentle boiling)

Indicator = $KMnO_4$ itself – self indicator

End point = From colorless to pale pink color

Trials →	**1**	**2**	**3**
Final burette reading			
Initial burette reading			
Volume of $KMnO_4$ added (mL)			

Agreeing value, V_1 =_____mL

ii) Estimation:

Weight of weighing bottle with pyrolusite ore, W_1 = _____ g.

Weight of empty weighing bottle, W_2 = _____ g.

Weight of pyrolusite ore, W = (W_1 - W_2) = _____ g.

Back titration:

Solution taken in the burette = Standard $KMnO_4$ solution

Solution taken in the conical flask = 25 mL of the experimental solution +
1 test tube dilute H_2SO_4 (Heat to gentle boiling)

Indicator = $KMnO_4$ itself - self indicator

End point = From colorless to pale pink color

Trials →	**1**	**2**	**3**
Final burette reading			
Initial burette reading			
Volume of $KMnO_4$ added (mL)			

Agreeing value, V_2 = _____ mL

MnO_2 present in $(W_1 - W_2)$ g of pyrolusite $\equiv$ 10 $(V_1 - V_2)$ mL of 0.1 N $KMnO_4$ solution

1000 mL of 1 N $KMnO_4 \equiv$ 43.47 g MnO_2

$\therefore$ 10 $(V_1 - V_2)$ mL of 0.1N $KMnO_4$ $= \dfrac{10\,(V_1 - V_2) \times 43.47 \times 0.1 \text{ g } MnO_2}{1000 \times 1}$

$= \dfrac{\times 43.47 \times 0.1}{1000}$

$= \dfrac{}{} = X$ g

$\therefore$ Percentage of MnO_2 in the given sample of pyrolusite $= \dfrac{X \times 100}{(W_1 - W_2)}$

$= \dfrac{\times 100}{}$

$= \dfrac{}{}$

Review Questions:

1. Justify statement; The end point is detected without the use of an indicator in the estimation of MnO_2 in pyrolusite.
2. Why is titration to estimate MnO_2 in pyrolusite conducted in the hot condition and in acid medium?
3. Mention two practical applications of MnO_2
4. Write the reactions involved when oxalic acid is added to manganese dioxide under acidic conditions.
5. Explain why the reaction between acetic acid and potassium permanganate become faster as it proceeds.

Experiment No.: 6 **Date:**

AMMONIA NITROGEN IN A FERTILIZER

Aim of the experiment:

To determine the percentage of ammonia nitrogen in the given sample of fertilizer using approximately 1 N NaOH solution and a standard HCl acid solution of 0.1 N

Background information:

Fertilizers are substances that are added to soil to increase its fertility for the healthy growth of plants. The soil will become barren and infertile without these plant foods. These are mixtures of salts that contain the nutrients required for plant growth and help remove the deficiency of essential elements. The three major elements required are i) nitrogen to promote development of stems and leaves, ii) phosphorous to stimulate growth and to accelerate fruit and seed formation and iii) potash to the development of starches, sugars and fibres. The different classes of fertilizers include nitrogenous fertilizers (urea, ammonium sulfate, ammonium nitrate) phosphatic fertilizers (superphosphate of calcium), potassium fertilizers (potassium sulfate, potassium chloride) and mixed fertilizers (N, P, K- fertilizers). These fertilizers are important industrial products and important in everyday life, just like cement or glass. Nitrogen is essential for plant growth, since it is a constituent of amino acids and proteins, building blocks of cells. The purpose of the present experiment is to determine the percentage of ammonia nitrogen in the given nitrogenous fertilizer sample, volumetrically by excess of alkali method

Principle and outline:

Nitrogen present in ammounium salt is known as ammonia nitrogen. e.g. Ammonium sulphate. $(NH_4)_2SO_4$, diammonium phosphate, and $(NH_4)_2HPO_4$ When a known weight of such a fertilizer is boiled with a known excess of NaOH solution, ammonium, NH_4^+ ion of the fertilizer decomposes and escapes as NH_3 gas with steam.

$$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3\uparrow + H_2O + Na_2SO_4$$

The solution should be boiled until the decomposition of ammonium fertilizer is complete, as indicated by the absence of NH_3 in the steam. NaOH equivalent to NH_3

liberated is consumed during this reaction. Unreacted NaOH left over in the solution is determined by *back titration* with standard hydrochloric acid. The standard hydrochloric acid needed to titrate the same volume of NaOH solution used for boiling with the weighed sample of fertilizer is determined by *blank titration*. The difference between the blank and back titre values gives the volume of standard acid equivalent to ammonia nitrogen present in the fertilizer sample.

According to the above equation: 2 molecules of ammonia ≡ 2 atoms of nitrogen
≡ 2 molecules or 2 equivalents of NaOH

∴ Equivalent weight of ammonia = Molecular weight of NH_3 = 17
Equivalent weight of nitrogen = Atomic weight of nitrogen = 14

This is the titration of a strong base (NaOH) with a strong acid (HCl). Hence any acid-base indicators like phenolphthalein, methyl orange and methyl red are suitable. Methyl red indicator, which has yellow color in alkaline solution and red color in acid solution, is more convenient than the other two.

NH_3 gas dissolved in water is basic to litmus. It changes red litmus paper to blue. Hence presence or absence of ammonia can be tested by holding a moist red litmus paper in the steam escaping from the boiling solution.

Procedure:

(i) Blank titration:

Pipette out 25 mL of the given approximately 1 N NaOH solution into a 250 mL standard flask. Make up to the mark with distilled water and shake well. Pipette out 25 mL of this solution into a conical flask and add 3 drops of methyl red indicator. Titrateit with the standard HCl acid solution taken in a burette, until the color changes from yellow to pinkish red. Repeat the titration to obtain agreeing value. Let it be V_1 mL.

(ii) Estimation:

Weigh accurately given fertilizer sample into a conical flask. Pipette out 25 mL of the given approximately 1 N NaOH solution into it. Place a glass funnel on the flask and gently boil its contents until NH_3 gas ceases to evolve. (A moist red litmus paper held in the escaping steam does not turn blue). Add distilled water to the flask now and then to

maintain the volume of the solution in the flask while boiling. Cool it and transfer quantitatively into a 250 mL standard flask. Make up to the mark with distilled water and shake well.

Back titration: Pipette out 25 mL of this solution into a conical flask. Add 3 drops of methyl red indicator and titrate with the same standard HCl acid solution, until color changes from yellow to pinkish red. Repeat the titration to obtain agreeing value. Let it be V_2 mL. 10 ($V_1 - V_2$) mL of the standard HCl acid solution is equivalent to the ammonia nitrogen contained in the weighed sample of the fertilizer.

Result:

Percentage of ammonia nitrogen in the given fertilizer sample = ——————.

Observation and calculations:

(i) Blank titration:

Solution in the burette = Standard HCl acid solution
Solution in the flask = 25 mL of diluted NaOH solution
Indicator = 3 drops of methyl red
End-point = Change of color from yellow to pinkish red

Trials →	**1**	**2**	**3**
Final burette reading			
Initial burette reading			
Volume of HCl added (mL)			

Agreeing value, V_1 = _____ mL

ii) Estimation:

Weight of weighing bottle with fertilizer, W_1 = ——————— g.

Weight of empty weighing bottle, W_2 = ——————— g.

Weight of fertilizer, $W = (W_1 - W_2)$ = ——————— g.

Back titration:

Solution in the burette = Standard HCl acid solution
Solution in the flask = 25 mL of experimental solution
Indicator = 3 drops of methyl red
End-point = Change of color from yellow to pinkish red

Trials →	**1**	**2**	**3**
Final burette reading			
Initial burette reading			
Volume of HCl added (mL)			

Agreeing value, V_2 = ———— mL

1000 mL of 1 N HCl acid ≡ 14 g. of ammonia nitrogen

∴ 10 (V_1-V_2) mL of 0.1 N $_{HCl}$ acid ≡ $\frac{10\,(V_1-V_2) \times 0.1 \times 14 \text{ g}}{1000}$ of ammonia nitrogen

∴ Weight of ammonia nitrogen in the weighed fertilizer sample = $\frac{10(V_1-V_2) \times 0.1 \times 14}{1000}$

= $\frac{\quad \times 0.1 \times 14 \text{ g.}}{1000}$

= ———— = X g.

∴ Percentage of ammonia nitrogen in the given fertilizer sample = $\frac{X \times 100}{(W_1 - W_2)}$

= ———— × 100

=

Review Questions:

1. What is meant by ammonia nitrogen in a fertilizer?
2. What does the failure of red litmus turning blue on boiling the fertilizer the sodium hydrogen indicate?
3. Name the indicator used in the determination of ammonia nitrogen in a fertilizer?
4. Write the equation for the decomposition of ammonium sulfate with sodium hydroxide.
5. Why is the blank titer value always greater than the back titer value?

Graph presentation:

The experimental data can be analyzed by plotting a graph that results in a straight line or a curve. These data shown graphically clearly represent the interrelationship between two variables and they provide a pictorial representation of results which is more readily comprehended than a set of tabular results. The plot is particularly useful for determining the end-points in potentiometric or conductometric titrations or the amount of analyte in the sample in colorimetric determinations. Remember the following rules for proper representation of data in graphical form.

1. Construction of the graph involves marking the points corresponding to the variables measured using a graph paper and a pencil. e. g. Plot the observed potentials (EMF values)/absorbance/ pH on the y-axis (*ordinate*) and the volumes of reagent added/the concentrations of the standard solutions (amount of analyte)on the x-axis (*abscissa*).

2. Draw a line through these data points that best represents the relationship between the two variables. A straightline plot/calibration curve will be obtained. Experimental data do not fall on a smooth curve but lie on either side of it when they are plotted because they contain measurement errors associated with the data. Draw a smooth curve as close to all the data points as possible. It is very important that it represents the ***best fit*** ["*weighted average*"] for the calibration data as the curve is fundamental to the accuracy of the method.
3. Results for unknowns are then interpolated from the calibration graph. Extrapolate a straight line beyond the range of the data that cuts the x-axis at a point corresponding to the volume of the titrant solution or calculate the slope of a straight line as appropriate.

4. The equivalence point is the volume of the solution added corresponding to the steepest portion of the curve in potentiometric titrations or in pKa determination using pH meter.

5. Note that the slope of a straight line is the same at all points where as the slope changes from point to point on a curve**. [**Slope***, m = ΔY/ΔX***]**

6. The graph should have a proper title or caption that explains the data being presented therein. e.g. A graph of the concentrations vs. absorbance in the determination of amount of copper or potential /volume curve for the titration of acetic acid vs. sodium hydroxide solution or conductometric titration curve for strong acid and strong base.

7. Label both the horizontal axis and the vertical axis of the graph with the variable associated with each and their appropriate units in which the variables are expressed.
8. Write the scale used on right hand top portion as follows:

   e.g. X- axis – 1cm = 0.5 mLY-
   axis – 1cm = 0.5 pH
9. Present the results obtained from the graph on the right hand bottom portion along with their proper units.
10. Do not attempt to draw the graph outside the boundaries corresponding to the maximum and minimum data values measured. Learn from your mistakes. Don't be afraid to ask questions. Chemistry books will expose you to new horizons.
11.

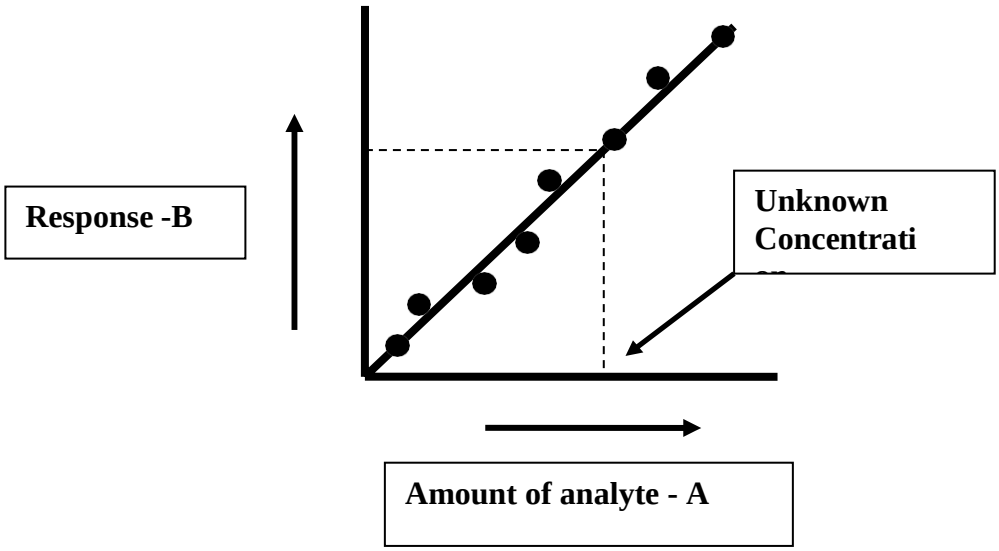


Fig.1. A typical (ideal) calibration curve of variable B vs variable A. The amount of an unknown can be determined from the graph as shown.

Experiment No.: 7 **Date:**

pK_a VALUE OF A WEAK ACID

Aim of the experiment:

To determine the pK_a value of a weak acid potentiometrically using a pH meter

Background information:

Potentiometric titration is an important electroanalytical technique and involves measurement of potential of a suitable indicator electrode as a function of titrant volume. In the acid-base titration, the pH of the solution rises gradually and then more rapidly. There is a sharp increase in pH for a very small quantity of base. Beyond the equivalence point, the pH increases only slightly on addition of excess base. Thepotential of an electrode depends upon the nature/composition of the electrodes (tendency to lose/gain of electrons), temperature (T) and concentration (C) of the electrolyte solution. A weak acid such as acetic acid, boric acid, phosphoric acid,nitrous acid, carbonic acid, is only partially dissociated into its constituent ions in solution. We define the pKa of an acid by pKa = – logKa where Ka = acid dissociation constant and the larger the value of pKa, the weaker is the acid. The pH meter is an electronic digital voltmeter scaled to read pH directly i.e. the potentiometer reading is automatically converted to give the pH of the test solution. The advantages of potentiometric method include the following; i) useful where there is no suitable indicator or color change difficult to ascertain ii) can be used in the titration of polybasic acids, mixtures of acids & mixtures of bases iii) it can be used where the process automation, with end-point data storage facility in a computer is required
iv) where the end-point obtained by the indicator is masked (colored, turbid or fluorescent) In this experiment, titration of weak acid (CH_3COOH) with strong base (NaOH) is carried out and the equivalence point is determined based on the change in pH value measured using a pH meter. The pKa value of an acid can be calculated using Handerson's equation {pH = pKa + log [salt]/[acid]}and the experimental titration curve obtained.

Principle and outline:

A weak acid, like acetic acid dissociates in its aqueous solution only slightly, as follows;

$$CH_3COOH + H_2O \rightleftarrows H_3O^+ + CH_3COO^-$$

The equilibrium constant of dissociation of the acid known as dissociation constant of the acid, Ka is given by:

$$K_a = \frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]}$$

The solution is considered to be very dilute and activity of water in very dilute solutions is assumed to be unity in the above equation.

$$\therefore [H_3O^+] = \frac{K_a\,[CH_3COOH],}{[CH_3COO^-]}$$

From the above equation, taking – log on both sides:

$$-\log [H_3O^+] = -\log Ka - \log \frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$\text{i.e. } pH = pKa + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

This is Henderson's equation. When acetic acid (titrate) is titrated with NaOH solution (titrant), pH of the titrated solution increases in accordance with the above equation; since concentration of sodium acetate, $[CH_3COO^-]$ increases and concentration of unreacted acetic acid, $[CH_3COOH]$ decreases as the titration progresses. When the acid is half - titrated,

$$[CH_3COO^-] = [CH_3COOH]$$

and hence $pH \equiv pK_a$

That is, pK_a of the acid is pH of the half-titrated acid solution or pH of the titrated solution at half way to the equivalence point.

Acetic acid can be titrated potentiometrically, using a pH sensitive glass electrode as indicator electrode and saturated calomel electrode as reference electrode both being connected to a pH meter to measure the pH of the titrated solution after each addition of NaOH solution from a burette. A graph is plotted taking volume of NaOH added along the X-axis and pH along the Y-axis. Volume of NaOH needed for the complete neutralization of the acid must be determined from the graph by dropping a perpendicular to the volume axis from the equivalence point (point of inflection or pointof maximum slope) on the graph. Volume of NaOH needed to neutralize half the amount of acetic acid is determined. pH of the titrated solution when this volume of NaOH is added is found out from the graph. It is the pK_a of acetic acid.

The pH meter should be standardized using a buffer solution of known pH in order to set the pH meter to read the pH of the titrating solution directly from the meter as accurately as possible. This is necessary as a glass electrode has to be standardized in a buffer solution of known pH due to different asymmetric potential values of different electrodes.

Procedure:

(i) Standardization of pH meter:

The combined electrode is dipped in the buffer solution of known pH taken in a beaker. The electrode is connected to the pH meter. Now the meter should show the pH of the buffer. If it does not show the correct pH, the control knob must be operated until the meter shows correct pH. Now the pH meter is standardized.

(ii) Potentiometric titration:

50 mL of the given weak acid is pipetted into a beaker. The combined electrode is dipped in the solution after rinsing it with distilled water. The electrode is connected to the pH meter and the pH of the acid is noted down before adding any NaOH to it.

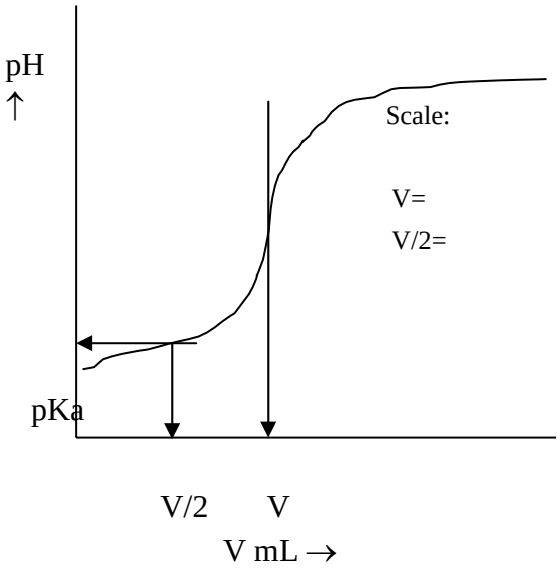
For the pilot reading, add exactly 1mL of NaOH from a semi-micro burette and stir the solution. Note down the pH of the resulting solution. Continue the addition of 1mL and note down the pH until comparatively a large change in pH is observed. Continue the addition of NaOH till 10 mL. Now, freshly pipette out 50 mL of the weak acid and record the pH of the solution after the addition of **0.1** mL portions of NaOH, in the volume range where large change in pH is observed. Continue to do so until change in pH becomes small again.

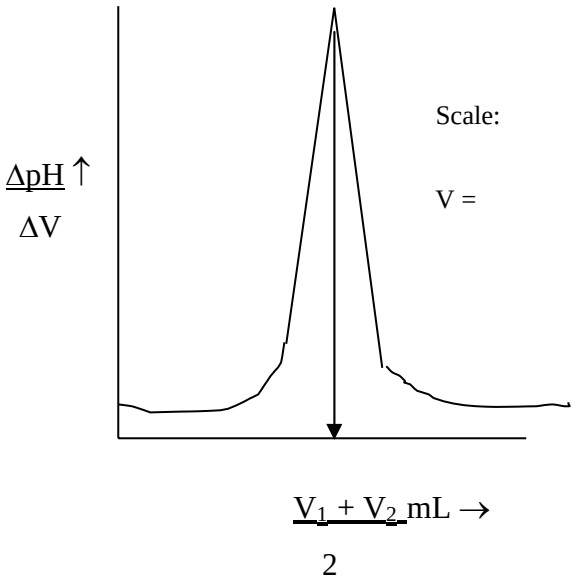
Now a graph is plotted taking the volume of NaOH along the X-axis and pH along the Y-axis. pK_a value is determined from the graph.

Result:

pKa value of acetic acid =

Graph:





Observation and calculations:

V Vol NaOH mL	**pH**	**ΔV** mL	**Δ pH**	**$\frac{\Delta pH}{\Delta V}$**	**$\frac{V_1 + V_2}{2}$** mL		**V** Vol NaOH mL	**pH**	**ΔV** mL	**Δ pH**	**$\frac{\Delta pH}{\Delta V}$**	**$\frac{V_1 + V_2}{2}$** mL
0.0		--	--	--	--							
1.0		1.0			0.5							
2.0		1.0			1.5							
3.0		1.0			2.5							
4.0		1.0			3.5							

Review Questions:

1. Name two strong acids and two strong bases used in the laboratory.
2. How are pKa and pH related to each other?
3. Write the ionization reaction of acetic acid.
4. What is a reference electrode? Give an example.
5. How do you determine pKa value of weak acid using pH meter?

Experiment No.: 8 **Date:**

CONDUCTOMETRIC TITRATION

Aim of the experiment:

To determine the strength of HCl and CH_3COOH by conductometric titration using standard NaOH solution and direct reading conductivity bridge

Background information:

Electrolytic conductivity is a measure of the ability of a solution to carry electric current through the migration of positive and negative ions under influence of an electric field. The conductivity of an electrolyte depends upon the type of the ions present and their concentrations. The overall conductivity of a solution, measured by using a conductivity cell, is the sum of individual contributions from the positive and negative ions. Conductometric titration is the determination of the equivalence point of a titration with the helpof conductivity measurements. The substitution of ions of particular conductivity by the ions of another value is the basis of conductometric titrations. During ionic reactions, the electrical conductivity of a solution may either increase or decrease depending upon the number of ions present and their mobility, charge, size, mass and the extent of solvation. The advantages of conductometric method include the following; i)useful for titrations of very dilute solutions, polybasic acids and that of weak acids and bases which do not give a sharp change of color with indicators ii) useful for colored solutions where suitable indicators are not available for volumetric methods iii) more accurate results are obtained because the equivalence point is determined graphically. The present experiment is used to determine thestrength of HCl and CH_3COOH using standard NaOH and conductivity bridge.

Principle and outline:

Reciprocal resistance(R) is conductance, L measured in siemens (mhos). Reciprocal resistivity (ρ) is conductivity, σ measured in siemens/ metre (mho/metre)

$$\text{i.e. } L = \frac{1}{R} = \frac{1}{\rho \times l/a} = \frac{\sigma a}{l}$$

$$\text{Hence } \sigma = L \times \frac{l}{a} = \frac{1}{R} \times \frac{l}{a}$$

l is the length of conductor in meter and a is its area of cross section in m^2.

Conductivity of a conductor can be calculated with the help of above formula, after determining the resistance of the conductor of known dimension (known a & l) experimentally, by Wheatstone bridge principle. Direct reading conductivity bridge available at present has simplified the experimental procedure.

Electrolytes do not possess fixed dimension. They are kept in conductivity cells to specify their dimension. A conductivity cell consists of a pair of platinized platinum foils of definite average area, 'a' rigidly fixed at a definite distance, 'l' apart. Thus l/a of a given conductivity cell has a definite value and it is known as cell constant, measured in m^{-1} (cm^{-1}). Conductance of an electrolyte is directly proportional to mobility of ions and number of ions present in unit volume. Mobility of H_3O^+ ions is about 5 to 7 times that of other cations and that of OH^- ions is about 3 to 5 times that of other anions.

It is possible to perform any titration conductometrically if the conductance of the titrating solution varies linearly with one slope before the equivalence point and with another slope after the equivalence point. The point of intersection of the two line marks the equivalence point. Conductance of the titrating solution varies due to two reasons; dilution and replacement of molecular species by ionic species or one ionic species by another.

Conductance varies linearly if the variation due to dilution is made zero. Therefore corrected conductance, L_c, must be calculated from the observed conductance, L_o, by applying the correction for dilution as shown in the formula given below.

$$L_C = \frac{(V + v) \times}{V} L_o$$

V is the volume of titrates and v is the total volume of titrant added. $L_c \cong L_o$, if v can be made negligibly small. This is achieved by using a titrant which is 10 to 100 times as concentrated as titrate. When HCl acid is titrated with NaOH (approx.10 times more concentrated than HCl), more mobile H_3O^+ ions are replaced by Na^+ ions due to the neutralization of H_3O^+ by OH^- of NaOH added.

$$\underbrace{H_3O^+ + Cl^-}_{\text{(HCl in titrate)}} + \underbrace{Na^+ + OH^-}_{\text{(NaOH of titrant)}} \rightarrow 2H_2O + \underbrace{Na^+ + Cl^-}_{\text{(NaCl in titrate)}}$$

Therefore, the conductance of the solution is maximum before any NaOH is added. It goes on decreasing due to the replacement of H_3O^+ ions by less mobile Na^+ ions of

NaOH. This continues until the equivalence point. NaOH added remains in solution after the equivalence point, as the solution does not contain HCl to neutralize NaOH. A highly mobile OH- ion of NaOH added increases the conductance of the solution after the equivalence point. Thus a V-shaped graph is produced when conductance of the solution is plotted with volume of NaOH. The point of inter-section marks the equivalence point of the titration.

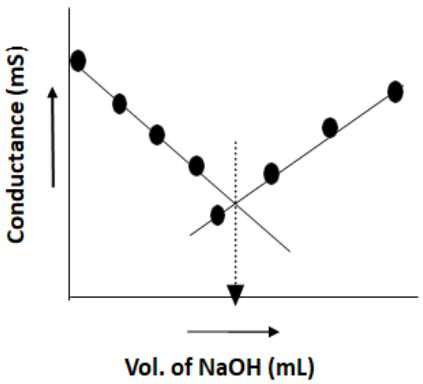
When CH_3COOH is titrated with NaOH the conductivity decreases initially. Since the concentration of H^+ ions in CH_3COOH is small, the conductance increases with the further addition of NaOH due to the formation of Na^+ & CH_3COO^- ions.

$$CH_3COO^- + H^+ + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + H_2O$$

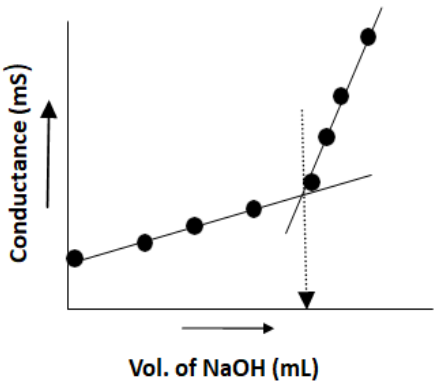
When the neutralization of acid is complete, further addition of NaOH produces excess of OH^- ions and the conductance of the solution increases more rapidly.

Graph:

Conductometric
Titration of strong acid vs strong base



Conductometric
Titration of weak acid vs strong base



V in the graph is the volume of NaOH needed to neutralize the HCl/CH_3COOH titrated.

$$\therefore N_{HCl/CH_3COOH} = \frac{N_{NaOH} \times V_{NaOH}}{V_{HCl/CH_3COOH}}$$

Procedure:

i) Determination of strength of HCl:

Pipette out 50 mL of HCl acid into a small beaker. Dip a clean conductivity cell rinsed with distilled water in the acid such that electrodes are completely immersed. A semi-micro burette filled with standard NaOH is positioned above the beaker containing the acid. Connect the conductivity cell to the conductivity bridge and switch on the bridge. Note down the conductance of the acid, before adding any NaOH to it. Run down the NaOH from the burette in 1 or 0.5 mL portions at a time and note down the conductance of the resulting solution after mixing the solution thoroughly. (The solution enclosed within the conductivity cell must be mixed thoroughly before noting down each reading). Continue the process until about 10 mL of NaOH is added. Draw a graph by plotting conductance, L along the Y-axis and volume, V of NaOH along the X-axis. Determine the end-point and read the volume, V of NaOH needed for the neutralization of HCl from the graph.

ii) Determination of strength CH_3COOH:

The above procedure is repeated with 50 mL of CH_3COOH instead of HCl.

Result:

(a) Volume of NaOH required by 50 mL HCl = _____ mL

(b) Normality of HCl = _____ N

(c) Volume of NaOH required by 50 mL of CH_3COOH = _____ mL

(d) Normality of CH_3COOH = _____ N

Observation and calculations:

i) Determination of strength of HCl:

Volume of HCl pipetted = 50 mL

Normality of NaOH = N

Volume of NaOH (in mL)	Conductance (in millimhos)	Vol of NaOH (in mL)	Conductance (in millimhos)	Vol of NaOH (in mL)	Conductance (in millimhos)
0.0		3.5		7.0	
0.5		4.0		7.5	
1.0		4.5		8.0	
1.5		5.0		8.5	
2.0		5.5		9.0	
2.5		6.0		9.5	
3.0		6.5		10.0	

Volume of NaOH added to get the equivalence point = mL

Normality of HCl = $\frac{N_{NaOH} \times V_{NaOH}}{V_{HCl}}$ = ——— N

ii) Determination of strength CH_3COOH:

Volume of CH_3COOH pipetted = 50 mL

Normality of NaOH = _____N

Volume of NaOH (in mL)	Conductance (in millimhos)	Vol of NaOH (in mL)	Conductance (in millimhos)	Vol of NaOH (in mL)	Conductance (in millimhos)
0.0		3.5		7.0	
0.5		4.0		7.5	
1.0		4.5		8.0	
1.5		5.0		8.5	
2.0		5.5		9.0	
2.5		6.0		9.5	
3.0		6.5		10.0	

Volume of NaOH added to get the equivalence point = mL

Normality of CH_3COOH = $\frac{N_{NaOH} \times V_{NaOH}}{V_{CH_3COOH}}$

= _____ N

Review Questions:

1. Give two differences between conductometric and volumetric titrations.
2. What is the principle of conductometric titration?
3. List two factors which influence the conductance of electrolyte solution.
4. Mention four different ions in the liquid when a solution of HCl in water conducts electricity
5. What is the unit of conductivity?
6. Sketch the shape of the curve for the conductometric titration of HCl vs NaOH

Experiment No.: 9 **Date:**

COLORIMETRIC ANALYSIS

Aim of the experiment:

To determine the concentration of copper in 50 mL of the given solution using photoelectric colorimeter

Background information:

A colorimeter is a light sensitive instrument used for determining the concentration of a solution by measuring the absorbance of particular wavelength of light. When light passes through a solution containing an appropriate absorbing species, some of the radiation is absorbed. Colorimetric analysis is a technique of determining the concentration of colored compounds in solution using visible light and it depends upon the measurement of quantity of light absorbed by a colored solution. Thus the absorption spectroscopy is a direct quantitative analysis technique for species which obey Beer's Law within acceptable limits. Copper, essential for plant, animal andhuman health, has a wider significance from research, therapeutic and toxicological considerations. Colorimetric method is commonly employed for its determination. The aim of the experiment is to determine the concentration of copper in 50 mL of the given solution using photoelectric colorimeter. The colorimetric determination of copper depends upon the production of intense blue color of the cupric ammonia complex whenammonia is added to a solution of a divalent copper salt. $[Cu^{2+}$ (aq) + 4 NH_3 (aq) → $[Cu[NH_3)_4]^{2+}$(aq)]. The learning objective of this experiment is to use colorimetric method to determine the concentration of an unknown colored solution. We can construct a calibration graph by measuring the absorption of light in a series of samples,starting with low concentration and proceeding to more concentrated solutions. This calibration graph can be used to determine the concentration of unknown samples. The principle of this quantitative analysis is that if light of a color (i.e. wavelength) absorbedby a sample, the amount absorbed will be proportional to the number of colored light- absorbing molecules.

Principle and outline:

The ammonium ion reacts with cupric ion to give the complex $[Cu(NH_3)_4]^{2+}$ which has an intense blue color. The quantity of light absorbed by these colored ions can be measured using a colorimeter.

Colorimetric analysis depends upon the measurement of quantity of light absorbed by a colored solution. Quantitative measurement of absorption is based on two fundamental laws: (1) Lambert's law and (2) Bear's law. Lambert's law relates to the transmission or transmittance and the thickness of the absorbing medium.

$I_t = I_o . 10^{-Kt}$ **(1)**

where I_t = intensity of the transmitted light, I_o = intensity of incident light, t = thickness of the light absorbing medium and K = a constant called absorptivity. Bear's law relates to the transmission or transmittance and the concentration of the colored constituent in solution.

$I_t = I_o . 10^{-K'C}$ **(2)**

where C = concentration of the colored constituent in solution and K = a constant.
Combining equations **(1)** and **(2),** we have;

$I_t - I_o\ 10^{-K'C}$ or $I_t/I_o = 10^{-Ect}$ **(3)**

Taking logarithms, $\log I_o/I_t = Ect$ **(4)**

where E is called molar absorptivity.

This is the fundamental equation in colorimetry and is known as Beer-Lambert Law. The ratio, $\log I_o/I_t$ is called absorbance of the light absorbing medium. The ratio of intensity of transmitted light and intensity of incident light is called Transmittance (T). Since 'E' is a constant and if thickness of the medium 't' is kept constant, then absorbance and transmittance are proportional to the concentration of colored constituent in solution. A series of solutions containing different known concentration of the colored constituent are prepared and their absorbance is measured in colorimeter using a suitable filter. The absorbance is plotted against the corresponding concentration. A straight line is obtained. From the graph the concentration of unknown solution can be found out by measuring under similar conditions, its absorbance.

Procedure:

Take a 3N ammonia solution in a cuvet. Place in the proper position in the colorimeter. Select a suitable filter and the adjuster is rotated to bring the scale reading to 100 percent transmittance or 'zero' absorbance. This is called 'blank setting'.

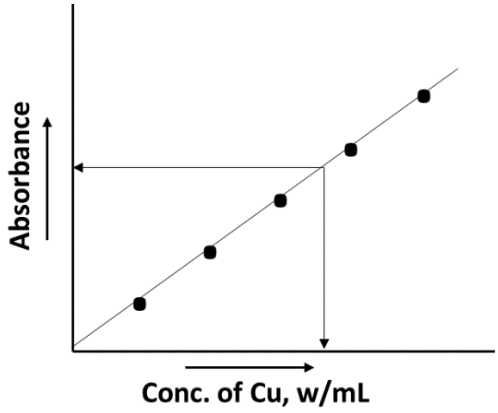
Weigh accurately about 1 g. of $CuSO_4.5H_2O$ crystals and transfer into a 250 mLstandard flask. Dissolve it in a little dilute H_2SO_4 and dilute up to the mark with distilledwater and shake well. The concentration of copper per milliliter is then calculated.

Prepare a series of standard copper sulfate solutions in 50 mL standard flasks bypipetting 5, 10, 15, 20, 25 mL of above standard copper sulfate solution separately. Add ammonia to each flask until a blue color is developed and then dilute up to the markwith 3N ammonia solution and shake well. Take each of this solution in the cuvet and measure the absorbance. The given copper solution in 50 mL standard flask is diluted with 3N ammonia solution up to the mark. The absorbance is measured for this solution of unknown concentration. Plot a graph of absorbance against correspondingconcentration copper. From this graph, calculate the concentration of copper in the given solution.

Result:

The weight of copper in 50 mL of the given solution =

Graph:



Observation and calculations:

Weight of weighing bottle + copper sulphate crystals, W_1 = g.
Weight of empty weighing bottle, W_2 = g.
Weight of copper sulphate crystals, $W = W_1 - W_2$ = g

Weight of $CuSO_4.5H_2O$ in one mL of the standard solution prepared,
W/250 = y = g

Weight of copper present in 1 mL of the standard solution prepared,
z = 63.54 **X** y **X** 1000/249.7
= mg

Sl. No.	Volume of standard copper solution pipetted in 50 mL standard flask V mL	Weight of copper in 1 mL of diluted solution in mg (z X V/50)	Absorbance
1	5		
2	10		
3	15		
4	20		
5	25		
6	30		
7	Unknown	Unknown	

From the graph, weight of copper in one mL of the solution = mg

Hence weight of copper in 50 mL of given solution = —**X** 50 = mg

Review Questions:

1. What is the principle of colorimetric analysis?
2. Write the mathematical formula of a straight-line graph of absorbance vs concentration.
3. How is the concentration of copper estimated from calibration graph in colorimetric analysis?
4. What is responsible for the intense blue color of the solution used to measure absorbance in colorimetric analysis?
5. What is the name of the sample cell used in measuring absorbance?
6. How do you carry out the blank setting in colorimetric analysis?

Experiment No.: 10 **Date:**

COEFFICIENT OF VISCOSITY OF LIQUID

Aim of the experiment:

To determine the coefficient of viscosity of a given organic liquid using Ostwald viscometer

Background information:

The viscosity of a liquid is the property of frictional resistance or internal friction offered that opposes the tendency of the liquid to flow when a stress is applied to it. It is due to the friction between neighboring particles in a liquid that are moving at different velocities. It depends on the size and shape of its particles and the intermolecular attractions in a liquid. The liquids which flow slowly such as glycerin, honey and castor oil are more viscous that those which flow quickly like water, petrol and benzene. It is a temperature dependent property and hence the measurements are carried out at constant temperature. In general, the viscosity decreases with increase in temperature. Superfluids exhibit zero viscosity at very low temperatures and solids like pitch has very high viscosity at room temperature. A liquid flowing through a cylindrical tube of uniform diameter at the macroscale is expected to move in the form of molecular layers at the microscale. The coefficient of viscosity is the tangential friction force per unit area required to maintain a unit velocity difference between any two successive layers of a liquid separated by a unit distance. The viscometer is an instrument used to determine viscosity by measuring the time required for a definite volume of liquid to flow through a capillary tube. The SI unit of viscosity is Pascal- second (Pa s) which is equivalent to $(N \cdot s)/m^2$ and the cgs unit is the poise. The aim of the present experiment is to determine relative viscosity of liquid with respect to water by Ostwald viscometer.

Principle and outline:

The measurement of viscosity by viscometer is based on Poiseulle's equation

$$\eta = \frac{\pi P r^4 t}{8Vl}$$

Where V = volume of liquid, η = viscosity, t = time, r = radius of capillary tube
l=length of capillary tube, P = hydrostatic pressure of liquid

If t_1 and t_2 are the times (in seconds) required to flow for equal volumes of two liquids through the same length of a capillary tube then from equation 1 we have

$$\frac{P_1}{P_2} = \frac{d_1}{d_2}$$

Therefore,

$$\frac{\eta_1}{\eta_2} = \frac{d_1}{d_2} \cdot \frac{t_1}{t_2}$$

Pressure of liquid = h.d. g

Since for two liquids h and g are same,

$$\frac{P_1}{P_2} = \frac{d_1}{d_2}$$

Therefore,

$$\frac{\eta_1}{\eta_2} = \frac{d_1}{d_2} \cdot \frac{t_1}{t_2}$$

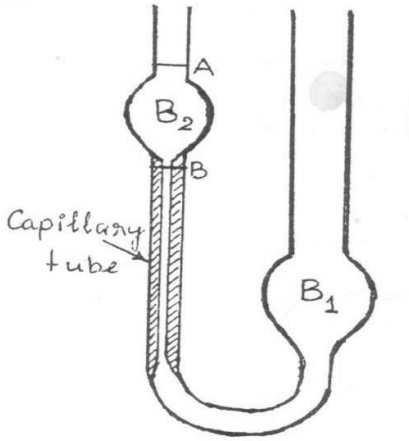
Where d_1 and d_2 are the densities of two liquids.

If η_1 and η_2 are the viscosities of the liquid and water respectively,

$$\eta_1 = \frac{d_1}{d_2} \cdot \frac{t_1}{t_2} \cdot \eta_2$$

Liquid **1** is the experimental liquid. Liquid **2** is the reference liquid, usually distilled water whose density and viscosity at lab temperature are known. This is the basis of determination of coefficient of viscosity of a liquid, using Ostwald viscometer whose diagram is shown below. It has a U shaped glass tube and in one arm, bulb B_2 is connected with a fine capillary. The lower end of the capillary is connected with a U- tube provided with a bulb B_1 in the second arm. The bulbs are necessary to maintain the hydrostatic pressure during flow of liquid. Through the capillary tube the liquid flows with measurable speed. There are two marks A and B above and below the bulb B_2. Theupper end of the bulb B_2 is attached with a rubber tube. The liquid flows under its own weight due to gravity.

The time t_1 seconds required by the given liquid and t_2 seconds required by distilled water contained between the marks A and B in the bulb B_2 to flow through the capillary tube of the viscometer are noted separately, using a stop-watch. Viscosity of the given liquid is then calculated using equation **(3)** with the knowledge of density d_1 of thegiven liquid, density, d_2 of distilled water and viscosity η_2 of the distilled water. The apparatus required for this experiment include Ostwald viscometer, stop watch and 15 mL pipette.



Ostwald viscometer

Procedure:

Pipette out 15 mL of the given liquid to the bulb B_1 of a thoroughly cleaned and dried Ostwald viscometer. Suck the liquid carefully into the bulb B_2 so that the level raises above the mark A. Allow it to flow to bulb B_1 through the capillary tube. Start the stop-watch when the liquid level touches mark A and stop it when the level touches mark B. Repeat this process thrice and note down average time. Clean and dry the viscometer and the pipette again. Pipet out the same volume of distilled water into bulb B_I and the average time of flow of distilled water is also noted down as explained above.

Result:

Coefficient of viscosity of the given liquid =

Observation and calculations:

Density of the given liquid, d_1= _____ kg/m^3

Density of water, d_2 = _____ kg/m^3

Viscosity of water = _____ N/m^2

Trial No.	Time of flow	
	for liquid t_1 seconds	**for water: t_2 seconds**
1.		
2.		
3.		
Average →		

Coefficient of viscosity of the liquid,

$$\eta_1 = \frac{d_1}{d_2} \cdot \frac{t_1}{t_2} \cdot \eta_2$$

= _____

= _____ N/m^2

Review Questions:

1. Define viscosity coefficient of a liquid. Give an example of a viscous liquid.
2. Why should the viscometer be dry before measurements are carried out?
3. What are the units of viscosity?
4. How does the viscosity of a liquid vary with rise in rise in temperature?
5. Why are bulbs necessary on the Ostwald viscometer?
6. List two factors affecting viscosity of a liquid.

Experiment No.: 11 **Date:**

FLAME PHOTOMETRIC DETERMINATION OF Na^+/ K^+ IONS

Aim of the experiment:

To determine the amount of sodium or potassium present in the given sample solution by flame photometric method.

Background information:

Sodium ion is the major cation of the extra cellular fluid whereas potassium is the major ion found inside the cells. The body maintains a delicate balance of these ions across the cellular membrane and any alteration in their normal values has significant physiological consequences. For example, an abnormal increase of potassium (hyperkalemia) or decrease of potassium (hypokalemia) can significantly affect the nervous system and heart, and if the levels become extreme, it can be fatal. In other words, an accurate determination of these ions in the body fluids can serve as important diagnostic tool.

Principle and outline:

When the solution containing a metallic compound of Na, K, Li, Ca and Ba is aspirated into a flame, a vapour containing the atoms of the metal may be formed. Some of these gaseous metal atoms may be raised to an energy level which is sufficiently high to permit the emission of radiation, which is characteristic of that metal(Eg, the characteristic yellow colour imparted to flames by compounds of sodium and Lilac colour imparted to flames by compounds of Potassium). This radiation can be measured by the detectors.

Instrumentation:

Air at a given pressure is passed in to the atomizer and the suction thus produced draws a solution of the sample in to the atomizer, where it joins the air stream as a fine mist and passes to the burner. Here in a small mixing chamber called nebulizer, the air meets the fuel supplied to the burner at a given pressure and the mixture is burnt. Radiations from the resulting flame passes through a lens and finally through an optical filter which permits only the radiation characteristic to the element under investigation to pass through the photocell. The output from the photocell is measured on a suitable digital readout system. The layout of a simple flame photometer is shown below.

Procedure:

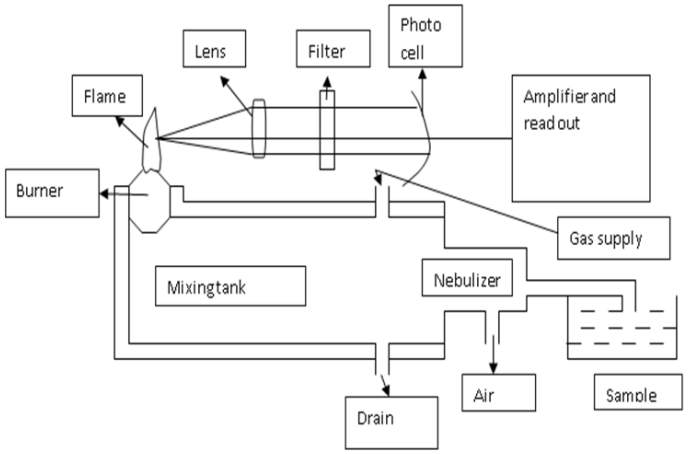
Estimation of Sodium and Potassium: Dissolve 2.542g Sodium chloride in 1liter distilled water in a graduated flask. This solution contains the equivalent of 1.0 mg Na (i.e.1000ppm). Dilute 100 ml of this stock solution to a liter to get 100 ppm solution. From this 100ppm solution prepare 2, 4, 6, 8 and 10 ppm sample of sodium ions in a 100ml std. flask by measuring same volume. Dilute up to the mark & shake well.

Dissolve 1.1902 g of Potassium chloride in 1liter distilled water in a graduated flask. This solution contains the equivalent of 1mg of K per ml (i.e.1000ppm). Dilute 100 ml of this stock solution to a liter to get 100 ppm solution. From this 100ppm solution prepare 2, 4, 6, 8 and 10 ppm sample of potassium ions in a 100ml std. flask by measuring same volume. Dilute up to the mark & shake well.

Instrumental procedure:

- Switch on the compressor, Dip the atomizer capillary tube in distilled water
- Switch fuel supply from fuel source and ignite the flame through ignition window
- Do fine adjustment of fuel flow with help of gas control valve to get stable flame having well defined cones.
- Display: Ready→ SETUP (Anyone out of 40 options)) →SET FLAME (select filter Na or K) → No. of STDS (enter desired number of std prepared/5)→ Dilution factor (ok)→ RUN
- Calibrate stds→Follow the instruction in the display during the RUN by aspirating distilled water and standard solutions→ Calibration OVER is displayed
- START SAMPLE ANALYSIS→ Name→RUN→ DISPLAY Result→SAVE

Finally, reading of the test solutions also noted.



Results:

The amount of sodium or potassium present in the given sample solution is……. ppm

Review Questions:

1. What is flame photometry? Mention its applications in analytical chemistry.
2. What is the principle of flame photometry?
3. What are the processes that occur in the flame when sample is aspirated to it?
4. Mention the various components of flame photometer.
5. Explain the various components of flame photometer.
6. Mention colour of the light emitted by i) lithium ion, ii) sodium ion, iii) Potassium ion iv) calcium ion.

Experiment No.: 12 **Date:**

Colorimetric estimation of chemical oxygen demand of water

Aim of the experiment:

To determine the chemical oxygen demand in the given water sample using a photoelectric colorimeter.

Background information:

The chemical oxygen demand (COD) value is a measure of water quality, used to measure the amount of organic compounds in water. COD is used to determine the amount of organic pollutants found in surface water. It is a measure of amount of oxygen in water consumed for chemical oxidation of pollutants into carbon dioxide and water and is expressed in milligrams per liter (mg/L), which indicates the mass of oxygen consumed per liter of solution. This method covers the determination of COD in ground and surface waters, domestic and industrial waste waters.

Principle and outline:

COD determines the quantity of oxygen required to oxidise the organic matter in water or waste water sample under specific conditions of oxidising agent, temperature and time. The organic matter present in sample gets oxidized completely by potassium dichromate in the presence of sulphuric acid, silver sulphate and mercury sulphate to produce CO_2 and H_2O. Silver sulphate is used as a catalyst. $K_2Cr_2O_7$ is reduced to the chromic ion (Cr^{3+}) in this test. The most common interferent is the chloride ion. Chloride reacts with silver ion to precipitate silver chloride, and thus inhibits the catalytic activity of silver. Bromide, iodide, and any other reagent that inactivates the silver ion can interfere similarly. Such interferences are negative in that they tend to restrict the oxidizing action of the dichromate ion itself. Despite being very strong oxidant, dichromate does not oxidize chloride in aqueous solutions. However, in presence of sulfuric acid, chromyl chloride is formed as given below

$$Cr_2O_7^{2-} + 4\,NaCl + 6\,H_2SO_4 \longrightarrow 2\,KHSO_4 + 4\,NaHSO_4 + 3\,H_2O$$

The interference of chloride can be reduced by adding mercury sulfate:

$$Hg^{2+} + 2Cl^- \longrightarrow HgCl_2$$

The sample is refluxed with a known amount of potassium dichromate in the sulphuric acid medium. When a sample is digested, the dichromate ion oxidizes organic material in the sample. This results in the change of chromium from the hexavalent (VI) state to the trivalent (III) state. Both of these chromium species are colored and absorb in the

visible region of the spectrum. The dichromate ion ($Cr_2O_7^{2-}$) absorbs strongly in the 400 nm region, where the chromic ion (Cr^{3+}) absorption is much less. The chromic ion absorbs strongly in the 600 nm region. In 9*M* sulfuric acid solution, the approximate molar extinction coefficients for these chromium species are as follows: Cr^{3+} − 50 L/mole cm at 604 nm; $Cr_2O_7^{2-}$ − 380 L/mole cm at 444 nm; Cr3+ − 25 L/mole cm at 426 nm. The Cr^{3+} ion has a minimum in the region of 400 nm. Thus a working absorption maximum is at 440 nm and the excess of potassium dichromate is determined by measuring absorbance of solution at 440 nm using photoelectric colorimeter.

The absorbance of dichromate solution and digested sample is measured at 440 nm. The absorbance is found to decrease in digested sample as the amount of dichromate decreases during digestion. The difference between these absorbance values is the amount of dichromate consumed during digestion. According Beer-Lambert's law,

$$\text{Absorbance } A = \varepsilon cl$$

Where ε is molar extinction coefficient, c is concentration and l is the path length of radiation passing through the sample. Using absorbance, molar extinction coefficient and path length of radiation the concentration of potassium dichromate consumed during digestion could be determined. The dichromate consumed by the sample is equivalent to the amount of O_2 required to oxidise the organic matter.

Procedure:

Preparation of Blank solution: Pipette out 25 mL of distilled water into the flask, followed by 25 mL of 0.25 M $K_2Cr_2O_7$ solution and 25 mL of conc. sulphuric acid. Mix it well.

Preparation of sample: Pipette out 25 mL of water sample into the conical flask. Add about 500 mg of $HgSO_4$, 25 mL of conc. sulphuric acid, 1 g of silver suphate and few glass beads. Then pipette out 25 mL of 0.25 M $K_2Cr_2O_7$ solution into it. Mix well and connect the reflux condenser and turn on cooling water. Reflux the mixture for 2 hours. After cooling down collect the sample and measure the absorbance values of blank solution and digested sample using colorimeter at 440 nm. The difference between absorbances of a given digested sample and the blank is a measure of the sample COD.

Result:

The COD of water sample is = mg/L

Observation and Calculation

Absorbance of Blank solution A_{Blank} =

$$A_{Blank} = \varepsilon cl$$

Concentration of $K_2Cr_2O_7$ in 75 mL of blank solution = 25×0.25/75 = 0.08 M

No of mols of $K_2Cr_2O_7$ = Molarity × Volume (L) = $0.08 \times 0.075 = 6\times10^{-3}$

1 mol of $K_2Cr_2O_7$= 294 g

6×10^{-3} mol of $K_2Cr_2O_7 = 249\times6\times10^{-3} = 1.494$ g

$$\varepsilon = \frac{\text{A Blank}}{cl} = \frac{\text{A Blank}}{1.494\times1} = \quad \text{L/gcm}$$

Absorbance of Digested water sample A_{sample} =

Absorbance Potassium dichromate utilized for oxidation $A = A_{Blank} - A_{sample}$

$$A = \varepsilon cl$$

$$c = \frac{A}{\varepsilon l}$$

$$c_{\text{ sample}} = \frac{A}{\varepsilon * 1} = \quad \text{\_\_\_\_\_} \quad = \quad \text{g/L}$$

Since the dichromate consumed by the sample is equivalent to the amount of oxygen required to oxidise the organic matter.

1 mol of $K_2Cr_2O_7$ consumed ≡ 48* g of Oxygen

[* 1 M of $K_2Cr_2O_7$ ≡ 294 g of $K_2Cr_2O_7$ in 1 liter of solution

1 N $K_2Cr_2O_7$ ≡ 49 g of $K_2Cr_2O_7$ in 1 liter of solution

1 equivalent of $K_2Cr_2O_7$ ≡ 1 equivalent of O ≡ 8 g of O

49 g of $K_2Cr_2O_7$ ≡ 8 g of O

294 g $K_2Cr_2O_7$ ≡ 48 g of O]

294 g of $K_2Cr_2O_7$ = 48 g of O

Csample g/L of $K_2Cr_2O_7$ = ?

Concentration of oxygen in water sample = $\frac{Csample \times 48 \times 1000}{294}$ =

= mg O_2 per L

The COD of water sample is = mg/L

Review Questions:

What is COD of water?
What are the products formed after COD analysis?
What is the function of $K_2Cr_2O_7$ in COD analysis?
Why is 440 nm filter is used for the measurement of absorbance in COD analysis?