



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 2019-2020.

Date:

Signature
Faculty in Charge

Signature
Head of the Department

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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%)

<i>Continuous evaluation</i> = 10/lab session	60
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➤ End-semester examination (40%)

- | | |
|--|----|
| • Written examination: Duration: 1/2 h, | 15 |
| • Performance of experiment:
Duration: 2.5h | 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 the 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 positive mental attitude.
- ✓ Invest time and energy to read the laboratory manual and related books. Follow the recommended procedures in the laboratory manual.
- ✓ Practice to produce a better written answer in the language of a particular subject.
- ✓ Compete with 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 do not come in contact with any chemicals.
- ✓ Wash your hands thoroughly with soapy water at the end of the laboratory period.

ALKALIMETRIC TITRATION

Aim of the experiment:

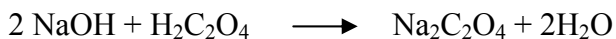
To estimate the amount of oxalic acid crystals dissolved per litre of the given solution using approximately decinormal sodium hydroxide solution and pure crystals of oxalic acid

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 and exhibits apparently strong links to the remaining laboratory experiments. The concentration of the analyte is determined from the stoichiometry of the reaction and the volume 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.



One molecule of oxalic acid = 2 molecules of NaOH
= 2 equivalents of NaOH

Equivalent weight of oxalic acid crystals $[\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}] =$

$$\frac{\text{Molecular weight}}{2} = \frac{126}{2} = 63$$

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 (pH range: 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. Appearance of 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

$$\begin{aligned}\text{Strength of the oxalic acid (OA) solution prepared, } N_{OA} &= \frac{W \times 4}{\text{Equivalent weight}} \\ &= \frac{\quad \times 4}{63} \\ &= \text{_____ N}\end{aligned}$$

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.

$$\begin{aligned} \text{Strength of the given NaOH solution } N_{\text{NaOH}} &= \frac{V_{\text{OA}} N_{\text{OA}}}{V_{\text{NaOH}}} = \frac{25 N_{\text{OA}}}{V_{\text{NaOH}}} \\ &= \\ &= \text{_____ N} \end{aligned}$$

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, $V_{\text{NaOH}} = \text{_____ mL}$

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

$$\begin{aligned} \text{Strength of the given oxalic acid solution, } N_{\text{OA}} &= \frac{V_{\text{NaOH}} N_{\text{NaOH}}}{V_{\text{OA}}} = \frac{V_{\text{NaOH}} N_{\text{NaOH}}}{25} \\ &= \\ &= \text{_____ N} \end{aligned}$$

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

$$\begin{aligned} &= N_{\text{OA}} \times 63 \\ &= \\ &= \text{_____ g} \end{aligned}$$

Review Questions:

1. Define 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?

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

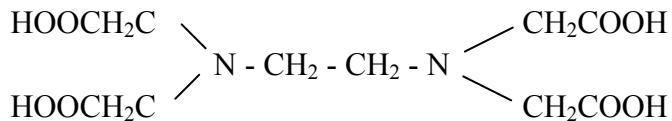
Background information:

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 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 experiment is 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:

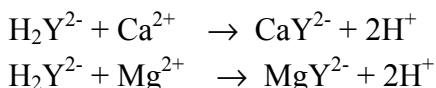
Water containing soluble salts (bicarbonates, chlorides and sulphates) of calcium and magnesium (less frequently iron and aluminum) is called hard water. Bicarbonates produce temporary hardness, while chlorides and sulphates produce permanent hardness. Temporary and permanent hardness together are called total hardness. 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;



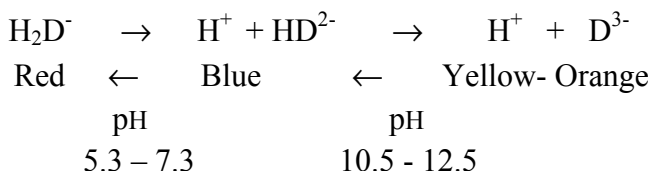
EDTA, $\text{H}_4\text{Y}(\text{H}_4\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2)$ is insoluble in water. Its disodium salt, $\text{Na}_2\text{H}_2\text{Y}$ is readily soluble in water. Analar material of the salt is in dihydrate form: $\text{Na}_2\text{H}_2\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$. (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.

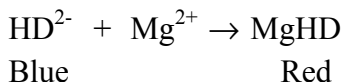
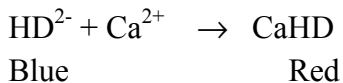


Removal of H^+ ions produced increases the stability of the complex ions formed. This is achieved by maintaining pH of the solution in basic range using an appropriate buffer solution.

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.

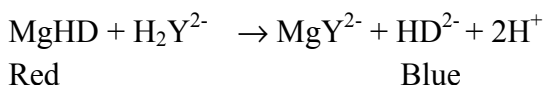
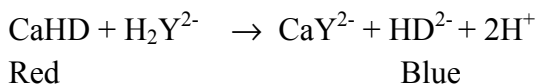


It exists as HD^{2-} in the pH range 7-11, exhibiting blue color. Many metal ions like Mg^{2+} & Ca^{2+} form red colored soluble complex ions with HD^{2-} .



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.



NH_4OH - NH_4Cl buffer is used to maintain the pH at 10 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 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 standardised. 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 is 100 g/mol 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 slowly till the solid completely dissolves. Neutralise the solution with NaOH solution till a white precipitate is formed. Dissolve the precipitate in 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 $\text{NH}_2\text{Cl-NH}_4\text{OH}$ 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 $\text{NH}_4\text{Cl} - \text{NH}_4\text{OH}$ 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 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 $\text{NH}_4\text{Cl-NH}_4\text{OH}$ 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 $\text{NH}_4\text{Cl-NH}_4\text{OH}$ 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

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

$$\equiv W/10 \text{ g of CaCO}_3$$

$$\therefore 1 \text{ mL of EDTA solution} \equiv \frac{W}{10} \times \frac{1}{V_1} \text{ g of CaCO}_3$$

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

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

$$\equiv \left[\frac{W}{10} \times \frac{1}{V_1} \right] \times V_2 \text{ g of CaCO}_3$$

$$\equiv \text{_____ g} = X \text{ g}$$

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. What is hardness of water due to?
5. How do you express the total hardness of water?
6. Differentiate between temporary and permanent hardness of water.

ANALYSIS OF COPPER IN BRASS

Aim of the experiment:

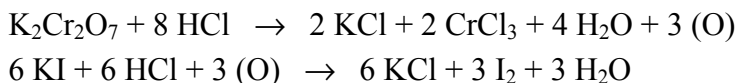
To estimate the percentage of copper in the given sample of brass using a solution of sodium thiosulfate of approximately 0.05 N and a solution of potassium dichromate in a 250 mL standard flask which on dilution up to the mark becomes exactly 0.05 N.

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 an engineering materials next to steel 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. It is 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.

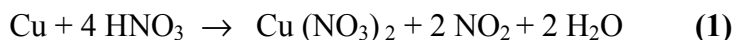
Principle and outline:

Given sodium thiosulfate solution is standardised 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.

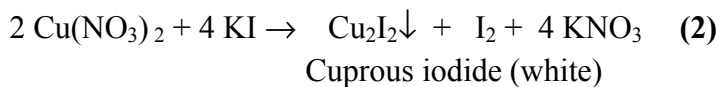


Liberated I_2 is titrated with sodium thiosulfate solution using starch solution near the end-point. Color changes from dark blue to bright green. This is due to the presence of $CrCl_3$ in the solution.

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.

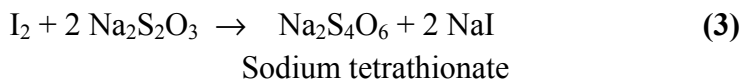


Cupric nitrate, $Cu(NO_3)_2$ liberates equivalent quantity of iodine by oxidation when excess KI is added to the brass solution.

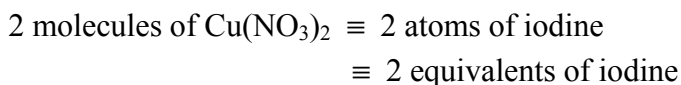


Iodine is sparingly soluble in water. It dissolves readily in KI solution forming tri iodide, I_3^- ions. Hence excess KI solution should be added to dissolve liberated iodine. The titration should not be prolonged unnecessarily as iodine vaporizes and escapes from the solution. By estimating the amount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

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



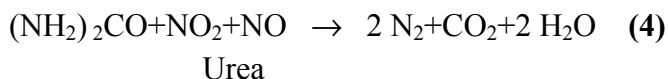
According to the equation 2,



\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 .



(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 $\text{Cu}(\text{OH})_2$ 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 $\text{Na}_2\text{S}_2\text{O}_3$ 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 $\text{Na}_2\text{S}_2\text{O}_3$ solution, resulting in a higher titre value. Hence starch indicator is to be added when the solution in the flask is faintly yellow which indicates low concentration of iodine.

Procedure:

(i) Standardisation of sodium thiosulfate solution:

Make up to the mark $\text{K}_2\text{Cr}_2\text{O}_7$ solution given in 250 mL standard flask. Shake well for uniform concentration. Pipette out 25 mL of this 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 $\text{Na}_2\text{S}_2\text{O}_3$ 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. $\text{Na}_2\text{S}_2\text{O}_3$ solution is standardised by this method.

(ii) 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 to lose any part of the solution. Dilute this solution with a little distilled water. Add about 1g 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 transfer washings 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 standardised 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) Standardisation of $\text{Na}_2\text{S}_2\text{O}_3$ solution:

Solution taken in the burette = Given $\text{Na}_2\text{S}_2\text{O}_3$ solution

Solution taken in the flask = 25 mL of $\text{K}_2\text{Cr}_2\text{O}_7$ 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

$$\begin{aligned}
 \therefore \text{Strength of given Na}_2\text{S}_2\text{O}_3 \text{ solution} &= \frac{25 \times 0.05}{V_{\text{Thiosulfate}}} \\
 &= \underline{25 \times 0.05} \\
 &= \text{_____ N}
 \end{aligned}$$

(ii) 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 $\text{Na}_2\text{S}_2\text{O}_3$ 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, $V_{\text{Na}_2\text{S}_2\text{O}_3} = \text{_____ mL}$

$$\begin{aligned}
 \therefore \text{Strength of copper in brass solution, } N_{\text{Cu}} &= \frac{V_{\text{Thiosulphate}} \times N_{\text{Thiosulphate}}}{25} \\
 &= \frac{X}{25} \\
 &= \text{_____ N}
 \end{aligned}$$

$$\begin{aligned}
 \therefore \text{Weight of copper in the whole of 250 mL of the solution} &= \frac{N_{\text{Cu}} \times 63.57}{4} \\
 &= \frac{\quad \times 63.57}{4} \\
 &= \text{_____} = X \text{ g}
 \end{aligned}$$

$$\begin{aligned}
 \therefore \text{Percentage of copper in brass} &= \frac{X \times 100}{(W_1 - W_2)} \\
 &= \text{_____} \times 100
 \end{aligned}$$

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. Give the chemical composition of brass.
6. Write the balanced chemical reaction between brass solution and potassium iodide.

ANALYSIS OF IRON IN HEMATITE

Aim of the experiment:

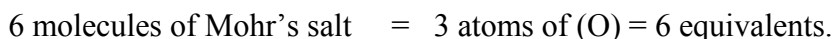
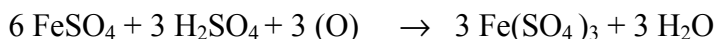
To estimate the weight of iron in hematite solution (FeCl_3) given in a 250 mL standard flask using approximately deci-normal $\text{K}_2\text{Cr}_2\text{O}_7$ solution and pure crystals of Mohr's salt (internal indicator method)

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 ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) 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.

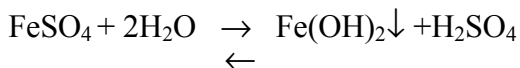
Principle and outline:

Mohr's salt is a double sulphate, $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ oxidises FeSO_4 of Mohr's salt to $\text{Fe}_2(\text{SO}_4)_3$ as follows;



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

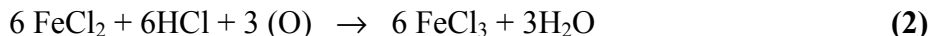
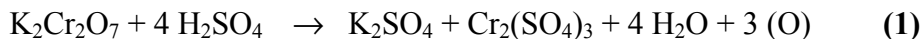
A standard solution (approx. 0.1N) of Mohr's salt must be prepared in a 250 mL standard flask by weighing accurately about $39.2/4 = 9.8$ g of the salt. FeSO_4 hydrolyses in aqueous solution as:



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

Given $\text{K}_2\text{Cr}_2\text{O}_7$ 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, $\text{K}_2\text{Cr}_2\text{O}_7$. FeCl_3 must be reduced to ferrous chloride, FeCl_2 that is a reducing agent and hence reacts with $\text{K}_2\text{Cr}_2\text{O}_7$, as shown below.



According to equation 1, 1 molecule of $\text{K}_2\text{Cr}_2\text{O}_7 \equiv 3$ atoms or 6 equivalents of oxygen.

$$\therefore \text{Equivalent weight of } \text{K}_2\text{Cr}_2\text{O}_7 = \text{Molecular weight of } \text{K}_2\text{Cr}_2\text{O}_7 / 6 = 294.18/6 = 49.03$$

According to equation 2, 6 molecules of $\text{FeCl}_2 \equiv 6$ molecules of FeCl_3
 $\equiv 6$ atoms of iron
 $\equiv 3$ atoms or 6 equivalents of oxygen

$$\therefore \text{Equivalent weight of } \text{FeCl}_2 = \text{Molecular weight of } \text{FeCl}_2 = 126.8$$

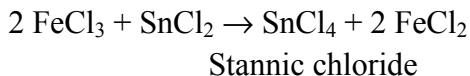
$$\text{Equivalent weight of } \text{FeCl}_3 = \text{Molecular weight of } \text{FeCl}_3 = 162.2$$

$$\text{Equivalent weight of iron} = \text{Atomic weight of iron} = 55.85$$

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 $\text{K}_2\text{Cr}_2\text{O}_7$, using diphenylamine as internal indicator.

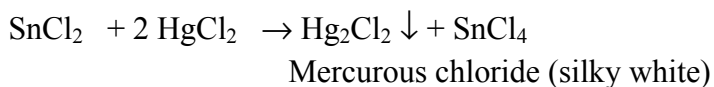
The precautions given below should be adopted in the experiment:

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



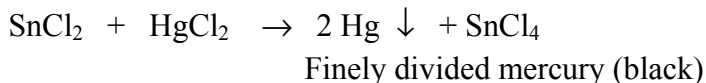
SnCl_2 solution should be added drop wise to the hot yellow colored solution containing FeCl_3 and concentrated HCl , until the solution becomes colorless and then one or two drops of SnCl_2 solution in excess to ensure complete reduction of FeCl_3 .

(ii) SnCl_2 is a strong reducing agent. It reduces $\text{K}_2\text{Cr}_2\text{O}_7$. If the solution is titrated with $\text{K}_2\text{Cr}_2\text{O}_7$ solution, before the destruction of unreacted SnCl_2 , both FeCl_2 and SnCl_2 present in the solution react with $\text{K}_2\text{Cr}_2\text{O}_7$, giving rise to higher titre value. Therefore unreacted SnCl_2 must be destroyed before titration. It is achieved by adding saturated HgCl_2 solution.



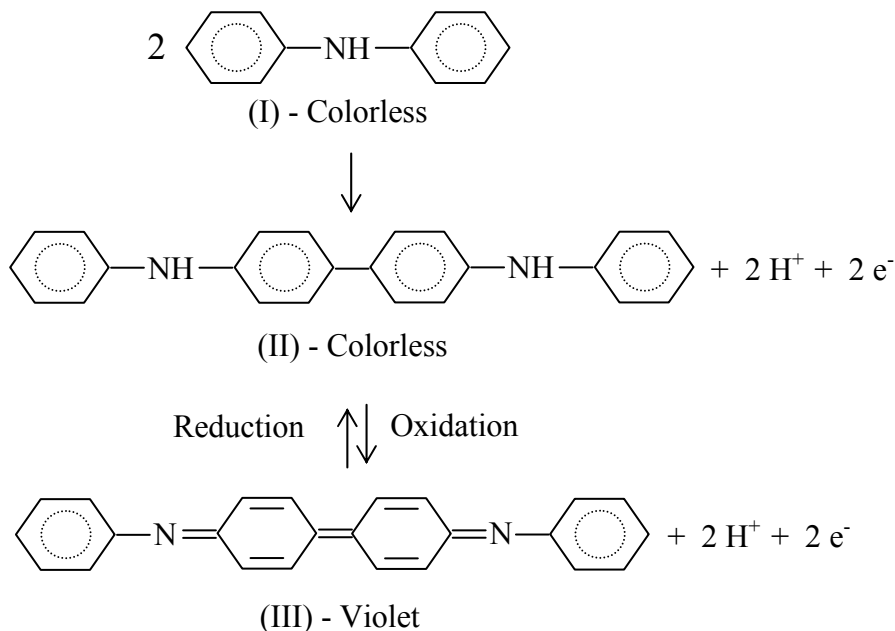
Hg_2Cl_2 does not react with $\text{K}_2\text{Cr}_2\text{O}_7$, even though it is also a reducing agent, since it is present as precipitate and not in solution.

(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 .



Finely divided mercury, being a good reducing agent reduces $\text{K}_2\text{Cr}_2\text{O}_7$. 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)



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 $\text{Cr}_2\text{O}_7^{2-}$ 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 of phosphoric 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, $[\text{Fe}(\text{PO}_4)_2]^{3-}$. 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 in a little dilute H_2SO_4 . Make the solution up to the mark with distilled water and shake well.

(ii) Standardisation of $\text{K}_2\text{Cr}_2\text{O}_7$ 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 $\text{K}_2\text{Cr}_2\text{O}_7$ 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 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 $\text{K}_2\text{Cr}_2\text{O}_7$ 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

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

(iii) Estimation of FeCl_3 :

Solution taken in the burette = Given $\text{K}_2\text{Cr}_2\text{O}_7$ 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 $\text{K}_2\text{Cr}_2\text{O}_7$ added (mL)			

Agreeing value, V _____ mL

$$\begin{aligned}\therefore \text{Strength of } \text{FeCl}_3 \text{ solution, } N_{\text{FeCl}_3} &= \frac{V_{\text{Dichromate}} \times N_{\text{Dichromate}}}{25} \\ &= \frac{\quad \times \quad}{25} \\ &= \text{_____ N}\end{aligned}$$

$$\begin{aligned}\therefore \text{Weight of iron present in the whole of 250 mL} &= \frac{N_{\text{FeCl}_3} \times 55.85}{4} \\ &= \frac{\quad \times 55.85}{4} \\ &= \text{_____ g}\end{aligned}$$

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.

MANGANESE DIOXIDE IN PYROLUSITE

Aim of the experiment:

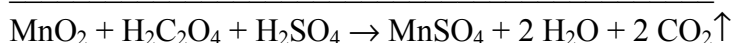
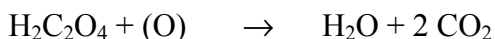
To estimate the percentage of MnO_2 in the given sample of pyrolusite, using approximately 1 N oxalic acid solution and a standard potassium permanganate solution of 0.1N

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.

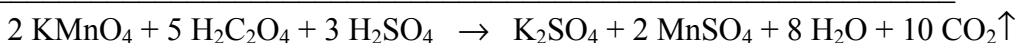
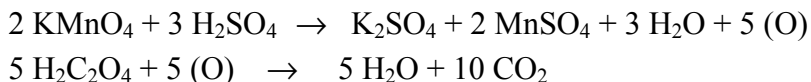


The unreacted oxalic acid left over is estimated by back titration with standard KMnO_4 solution. According to the above equation:

One molecule of $\text{MnO}_2 \quad \equiv \quad \text{One atom of oxygen}$
 $\quad \quad \quad \equiv \quad \text{Two equivalents of oxygen}$

$$\therefore \text{Equivalent weight of } \text{MnO}_2 = \frac{\text{Molecular weight}}{2} = \frac{86.94}{2} = 43.47$$

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



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 $\text{H}_2\text{C}_2\text{O}_4$ and KMnO_4 is very slow at room temperature. Hence the oxalic acid solution must be heated to $60^\circ - 80^\circ \text{C}$ 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 $-\text{Mn}^{2+}$ acts as catalyst for the reaction between $\text{H}_2\text{C}_2\text{O}_4$ 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 $\text{H}_2\text{C}_2\text{O}_4$.

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 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 obtain agreeing 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

MnO₂ present in (W₁ – W₂) g of pyrolusite \equiv 10 (V₁- V₂) mL of 0.1 N KMnO₄ solution

1000 mL of 1 N KMnO₄ \equiv 43.47 g MnO₂

$$\begin{aligned}\therefore 10 (V_1 - V_2) \text{ mL of } 0.1 \text{ N KMnO}_4 &= \frac{10 (V_1 - V_2) \times 43.47 \times 0.1 \text{ g MnO}_2}{1000 \times 1} \\ &= \frac{\times 43.47 \times 0.1}{1000} \\ &= \text{—————} = X \text{ g}\end{aligned}$$

$$\begin{aligned}\therefore \text{Percentage of MnO}_2 \text{ in the given sample of pyrolusite} &= \frac{X \times 100}{(W_1 - W_2)} \\ &= \text{—————} \times 100 \\ &= \text{—————}\end{aligned}$$

Review Questions:

1. Justify statement; The end point is detected without the use of an indicator in the estimation of MnO₂ in pyrolusite.
2. Why is titration to estimate MnO₂ in pyrolusite conducted in the hot condition and in acid medium?
3. How is the equivalent of MnO₂ calculated?
4. Mention two practical applications of MnO₂
5. Write the reactions involved when oxalic acid is added to manganese dioxide under acidic conditions.
6. Explain why the reaction between acetic acid and potassium permanganate become faster as it proceeds.

AMMONIA NITROGEN IN A FERTILIZER

Aim of the experiment:

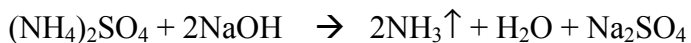
To determine the percentage of ammonia nitrogen in the given sample of fertilizer using approximately 1 N NaOH solution and a standard HCl acid solution of 0.1 N

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 ammonium salt is known as ammonia nitrogen. e.g. Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, diammonium phosphate, and $(\text{NH}_4)_2\text{HPO}_4$. 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.



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 a 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 \equiv 2 atoms of nitrogen
 \equiv 2 molecules or 2 equivalents of NaOH

$$\begin{aligned}\therefore \text{Equivalent weight of ammonia} &= \text{Molecular weight of NH}_3 = 17 \\ \text{Equivalent weight of nitrogen} &= \text{Atomic weight of nitrogen} = 14\end{aligned}$$

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.

NH₃ 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. Titrate it 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 V₁ 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 NH₃ 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, $V_2 = \text{_____ mL}$ 1000 mL of 1 N HCl acid \equiv 14 g. of ammonia nitrogen
$$\therefore 10 (V_1 - V_2) \text{ mL of } 0.1 \text{ N}_{\text{HCl}} \text{ acid} \equiv \frac{10 (V_1 - V_2) \times 0.1 \times 14}{1000} \text{ g of ammonia nitrogen}$$

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

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

$$= \text{_____} = X \text{ g.}$$

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

$$= \text{_____} \times 100$$

$$= \text{_____}$$

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. What is a fertilizer? Give an example of nitrogenous fertilizer.
4. What is the indicator used in the determination of ammonia nitrogen in a fertilizer?
5. What is the equation for the decomposition of ammonium sulfate with sodium hydroxide?
6. 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 straight line 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, $m = \Delta Y/\Delta X$]
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 mL
Y- 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.

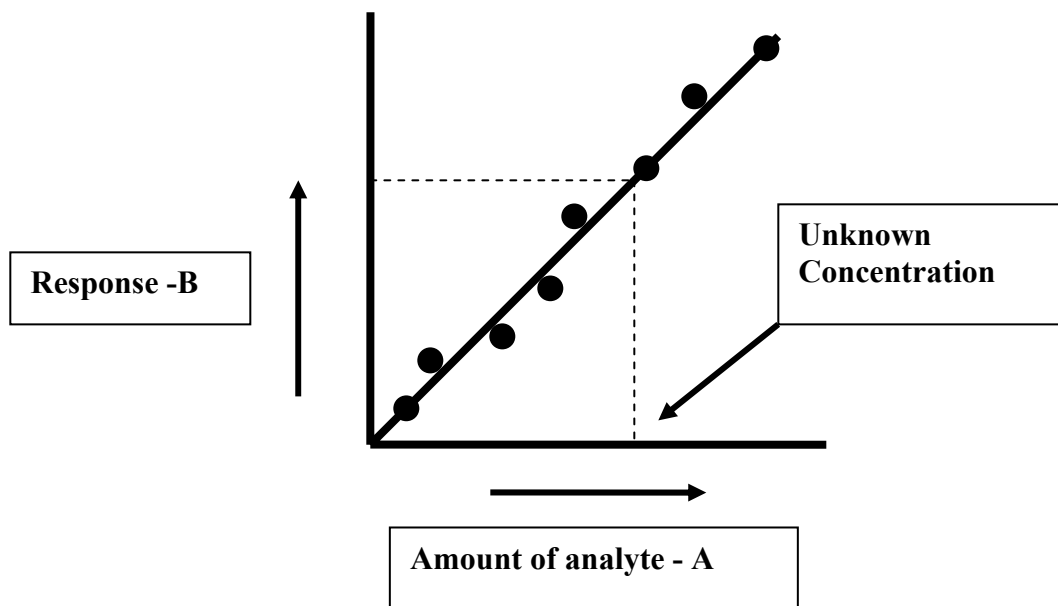


Fig.1. A typical (ideal) calibration curve of variable B vs variable A. The amount of an unknown can be determined from the graph as shown.

pK_a VALUE OF A WEAK ACID

Aim of the experiment:

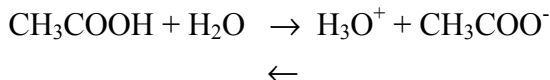
To determine the pK_a value of a weak acid potentiometrically using a pH meter

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. The potential 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 pK_a of an acid by $pK_a = -\log K_a$ where K_a = acid dissociation constant and the larger the value of pK_a, 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 (CH₃COOH) 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 pK_a value of an acid can be calculated using Handerson's equation $\{pH = pK_a + \log [salt]/[acid]\}$ and the experimental titration curve obtained.

Principle and outline:

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



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

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

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.

$$\therefore [\text{H}_3\text{O}^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

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

$$-\log [\text{H}_3\text{O}^+] = -\log K_a - \log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$\text{i.e. pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

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, $[\text{CH}_3\text{COO}^-]$ increases and concentration of unreacted acetic acid, $[\text{CH}_3\text{COOH}]$ decreases as the titration progresses. When the acid is half - titrated,

$$[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}]$$

and hence $\text{pH} \equiv \text{p}K_a$

That is, $\text{p}K_a$ of the acid is pH of the half-titrated acid solution or pH of the titrated solution at half way to the equivalence point or end-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 point of 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 standardised 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.

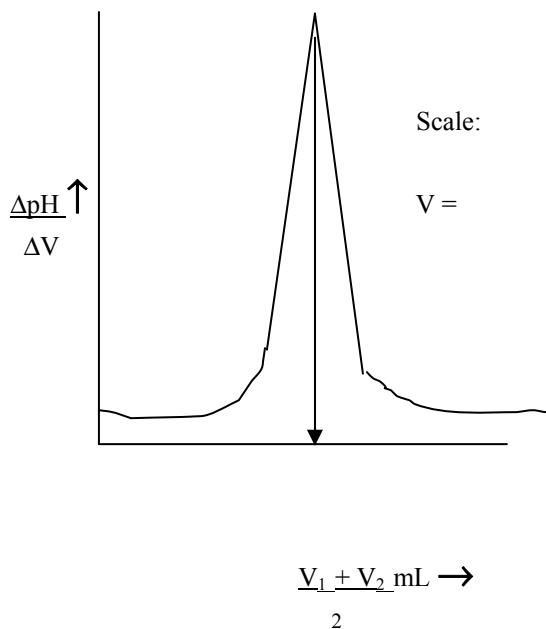
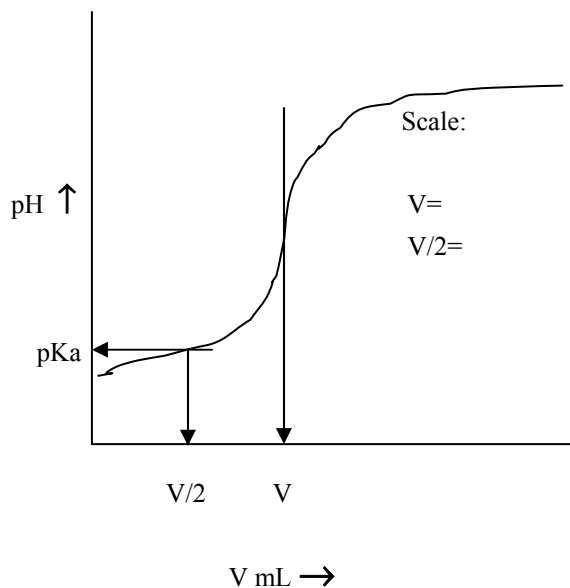
For the pilot reading, add exactly 1mL of NaOH from a semi-micro burette and stir the solution. Note down the pH of the resulting solution. Continue the addition of 1mL and note down the pH until comparatively a large change in pH is observed. Continue the addition of NaOH till 10 mL. Now, freshly pipette 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:

pK_a value of acetic acid =

Graph:



Observation and calculations:

[illegible]

Review Questions:

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

CONDUCTOMETRIC TITRATION

Aim of the experiment:

To determine the strength of HCl and CH₃COOH 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 end point of a titration with the help of 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 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 end-point is determined graphically and special care not required near the end-point iv) it can be used in case of polybasic acids where volumetric methods do not give correct end-points. The present experiment is used to determine the strength of HCl and CH₃COOH 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 m².

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.

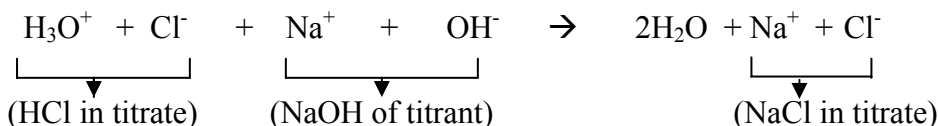
Electrolytes do not possess fixed dimension. They are kept in conductivity cells to specify their dimension. A conductivity cell consists of a pair of platinized platinum foils of definite average area, ' a ' rigidly fixed at a definite distance, ' l ' apart. Thus l/a of a given conductivity cell has 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 end-point and with another slope after the end-point. The point of intersection of the two line marks the end-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.

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

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.



Therefore, 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 CH₃COOH is titrated with NaOH the conductivity decreases initially. Since the concentration of H⁺ ions in CH₃COOH is small, the conductance increases with the further addition of NaOH due to the formation of Na⁺ & CH₃COO⁻ ions.

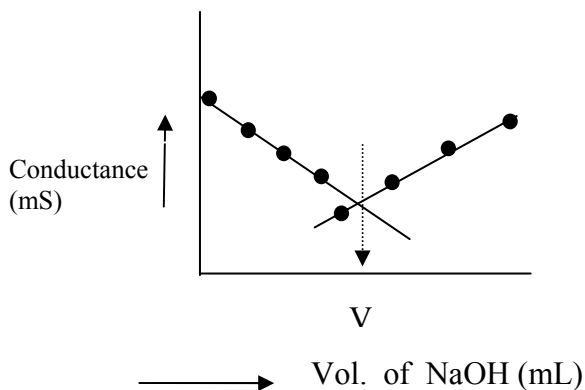


When the neutralization of acid is complete, further addition of NaOH produces excess of OH⁻ ions and the conductance of the solution increases more rapidly.

Graph:

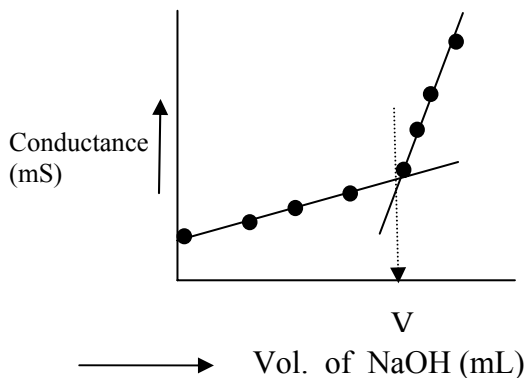
Conductometric

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/CH₃COOH titrated.

$$\therefore N_{\text{HCl/CH}_3\text{COOH}} = \frac{N_{\text{NaOH}} \times V_{\text{NaOH}}}{V_{\text{HCl/CH}_3\text{COOH}}}$$

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 end-point = _____ mL

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

ii) Determination of strength CH₃COOH:Volume of CH₃COOH 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 end-point = mL

$$\begin{aligned}\text{Normality of CH}_3\text{COOH} &= \frac{N_{\text{NaOH}} \times V_{\text{NaOH}}}{V_{\text{CH}_3\text{COOH}}} \\ &= \\ &= \text{—————N}\end{aligned}$$

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

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 and human 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 when ammonia is added to a solution of a divalent copper salt. $[\text{Cu}^{2+}(\text{aq}) + 4 \text{NH}_3(\text{aq}) \rightarrow [\text{Cu}(\text{NH}_3)_4]^{2+}(\text{aq})]$. 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) absorbed by 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 $[\text{Cu}(\text{NH}_3)_4]^{2+}$ 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.

$$I_t = I_o \cdot 10^{-Kt} \quad (1)$$

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.

$$I_t = I_o \cdot 10^{-K'C} \quad (2)$$

where C = concentration of the colored constituent in solution and K = a constant.

Combining equations (1) and (2), we have;

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

$$\text{Taking logarithms, } \log I_o/I_t = Ect \quad (4)$$

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:

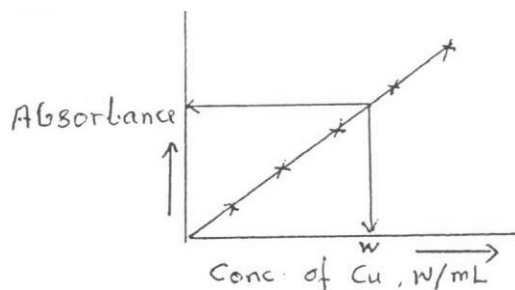
Take a 3N ammonia solution in a cuvet. Place in the proper position in the colorimeter. Select a suitable filter and the adjuster is rotated to bring the scale reading to 100 percent transmittance or 'zero' absorbance. This is called 'blanksetting'.

Weigh accurately about 1 g. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals and transfer into a 250 mL standard flask. Dissolve it in a little dilute H_2SO_4 and dilute up to the mark with distilled water 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 by pipetting 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 mark with 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 corresponding concentration 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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in one mL of the standard solution prepared,
 $W/250 = y =$ g

Weight of copper present in 1 mL of the standard solution prepared,
 $z = 63.54 \times y \times 1000/249.7$
 $=$ 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 ($z \times V/50$)	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 = $\text{---} \times 50 =$ 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?

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 than 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 have 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·s)/m² 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 Poiseuille's equation

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

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

$$\frac{\eta_1}{\eta_2} = \frac{P_1}{P_2} \cdot \frac{t_1}{t_2}$$

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,

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

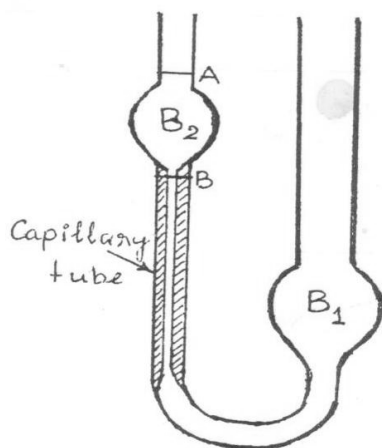
Where d_1 and d_2 are the densities of two liquids.

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 . The upper 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 the given 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_1 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 \rightarrow		

Coefficient of viscosity of the liquid,

$$\eta_1 = \frac{d_1^4}{d_2^4} \cdot \frac{t_1}{t_2} \cdot \eta_2$$

$$= \underline{\hspace{2cm}}$$

$$= \underline{\hspace{2cm}} \text{ N/m}^2$$

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.

ANALYSIS OF CHLORIDE IN WATER

Aim of the experiment:

To estimate the chloride content of the given sample of water using approximately 0.02 N silver nitrate solution and pure crystals of potassium chloride by argentometric method.

Background information:

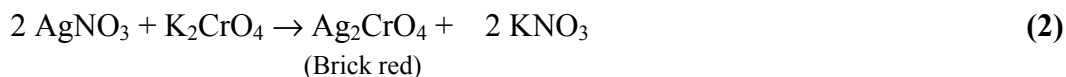
Water has an essential role in maintaining the plant and animal life since nearly all life processes depend on reactions occurring in an aqueous solution. It is a universal solvent that can dissolve many ionic and covalent compounds and acts as a good ligand with transition metal ions that makes water a substance of great importance. The nature of chlorides of the elements varies from mainly ionic to predominantly covalent and often occur in coordination complexes. Chloride is one of the major anions widely distributed in nature and they are present in water usually in combined form with calcium, magnesium, potassium or sodium. Chlorides are leached from various rocks into soil and water by weathering. Chloride is essential for aquatic and terrestrial species representing the main extra-cellular anion in animals including human beings. Chloride is necessary for human metabolism and the kidneys control the amount of chloride in blood. It is recommended that the total concentration of chloride in drinking water should not exceed 250 mg/L. The chloride concentration of more than 250 ppm in water imparts a peculiar taste making it unacceptable for drinking purposes. The purpose of the experiment is to determine chloride content of water sample by titrating it against standard silver nitrate (AgNO_3) solution using potassium chromate as indicator.

Principle and outline:

KCl reacts with AgNO_3 forming curdy white precipitate of AgCl.



AgNO_3 reacts with K_2CrO_4 forming a brick red precipitate of Ag_2CrO_4 .



When AgNO_3 solution is added to an aqueous solution containing both KCl and K_2CrO_4 , curdy white AgCl precipitates at first, since its solubility ($1.5 \times 10^{-3} \text{ g dm}^{-3}$ or $1.05 \times 10^{-5} \text{ mol dm}^{-3}$) is less than that of Ag_2CrO_4 ($2.5 \times 10^{-2} \text{ g dm}^{-3}$ or $7.5 \times 10^{-5} \text{ mol dm}^{-3}$). Brick-red Ag_2CrO_4 precipitates after the precipitation of Cl^- ions as AgCl is complete. Thus brick-red color due to Ag_2CrO_4 appears at the end-point of the titration.

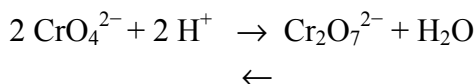
From the equation 1; One molecule of $\text{KCl} = 1$ molecule of $\text{AgNO}_3 = 1$ Equivalent
 \therefore Equivalent weight of $\text{KCl} = \text{its molecular weight} = 74.5$

Similarly, equivalent weight of $\text{NaCl} = \text{its molecular weight} = 58.5$

A standard solution of KCl is prepared in 250 mL standard flask by weighing accurately about 0.5 g. of the crystals. A known volume of this standard solution is titrated against AgNO_3 solution using K_2CrO_4 as the indicator. Thus, the given AgNO_3 is standardised.

The given water sample contains dissolved chloride salts and mineral acids. A known volume of water is treated with solid CaCO_3 to neutralise mineral acids and titrated against standardised AgNO_3 solution using K_2CrO_4 as indicator. From the titre value normality of water sample and hence chloride content can be calculated. Chloride content in water sample is expressed in ppm of sodium chloride.

This titration (Cl^- vs. AgNO_3 using K_2CrO_4 indicator) must be performed in neutral medium. In acidic medium CrO_4^{2-} ion changes to $\text{Cr}_2\text{O}_7^{2-}$ ion:



This solution will not contain CrO_4^{2-} ions to show the end-point. In alkali medium AgNO_3 precipitates as black $\text{Ag}(\text{OH})$ precipitate.

Procedure:**(i) Preparation of standard solution of KCl:**

Weigh accurately the given KCl crystals in weighing bottle into a 250 mL standard flask. Dissolve it in distilled water and make up to the mark and shake well for uniform concentration.

(ii) Standardisation of AgNO_3 solution:

Pipette out 25 mL of prepared KCl solution into a clean conical flask. Add 10 drops of 2 percent K_2CrO_4 solution as internal indicator. Titrate it against AgNO_3 solution taken in the burette. End point is marked by the appearance of reddish brown tinge which persists even after brisk swirling. Repeat the titration to get concordant values.

(iii) Estimation:

Pipette out 25 mL of water sample into a clean conical flask. Add about 1 g of solid CaCO_3 followed by 10 drops of K_2CrO_4 indicator. Titrate the solution against AgNO_3 solution as before. Repeat the titration to get agreeing values.

Result:

Chloride content in the given sample of water = _____ ppm NaCl or its equivalent.

Observation and calculations:**i) Preparation of standard KCl solution:**

Weight of weighing bottle + KCl crystals, W_1 = _____ g

Weight of the bottle after transferring, W_2 = _____ g

\therefore Weight of KCl crystals dissolved

per 250 mL solution, $W = (W_1 - W_2)$ = _____ g

\therefore Strength of KCl solution prepared = $\frac{(W_1 - W_2) \times 4}{74.5}$
 = $\frac{\quad \times 4}{74.5}$
 = _____ N

ii) Standardisation of AgNO_3 solution:

Solution taken in the burette = Given AgNO_3 solution

Indicator used = 10 drops of 2 percent K_2CrO_4 solution

End point = Appearance of pale reddish brown tinge.

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

Agreeing value, $V_{\text{AgNO}_3} = \text{_____ mL}$

$$\begin{aligned}
 \therefore \text{Strength of AgNO}_3 \text{ solution} &= \frac{25 \times N_{\text{KCl}}}{V_{\text{AgNO}_3}} \\
 &= \underline{25 \times} \\
 &= \text{_____ N.}
 \end{aligned}$$

iii) Estimation of chloride in water:

Solution taken in the burette = Given AgNO₃ solution

Solution taken in the flask = 25 mL of water sample + 1 g of solid CaCO₃

Indicator used = 10 drops of K₂CrO₄ solution

End point = Appearance of pale reddish brown tinge

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

Agreeing value, $V_{\text{AgNO}_3} = \text{_____ mL}$

$$\begin{aligned}
 \therefore \text{Strength of chloride in water} &= \frac{V_{\text{AgNO}_3} \times N_{\text{AgNO}_3}}{25} \\
 (N_{\text{Chloride}}) &= \underline{\underline{\frac{\times}{25}}} \\
 &= \text{_____ N}
 \end{aligned}$$

∴ Weight of chloride as NaCl per litre of the solution = $N_{\text{Chloride}} \times 58.5$

$$= \frac{\quad \times 58.5}{\quad}$$

$$= \frac{\quad}{\quad} = X \text{ g}$$

∴ Chloride content of water sample = $X \times 1000$

$$= \frac{\quad}{\quad} \times 1000 \text{ mg / dm}^3$$

$$= \frac{\quad}{\quad} \text{ ppm. of NaCl or its equivalent}$$

Review Questions:

1. What is a standard solution? Give normality equation.
2. Give balanced equation for the reaction of silver nitrate with potassium chloride and potassium chromate.
3. Why is silver nitrate solution generally stored in amber colored reagent bottles?
4. Why does silver nitrate combine first with potassium chloride in the water rather than with potassium chromate?
5. Name the indicator used to estimate the chloride content of water using argentometric method
6. How do you calculate the strength of chloride ions in water sample, if we know the normality?

ANALYSIS OF WHITE LEAD PIGMENT

Aim of the experiment:

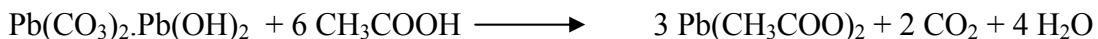
To estimate the percentage of lead in the given sample of white lead pigment

Background information:

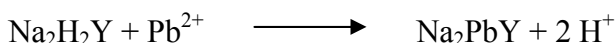
The pigments are an important class of industrial materials mainly used in the production of paints and paper. They are used in providing desired color, hiding power to cover the surface from grain & defects and in preventing the penetration of harmful UV light. Other functions of pigment as an essential constituent of paint include i) provide strength to paint ii) give aesthetic appeal to the paint film iii) provide resistance to paint film against abrasion and iv) increase weather resistance of the film. They are characterized by their low solubility in solvents/binders, chemical composition, covering power, optical and corrosion inhibiting properties. The particle size determines the ability of a given pigment to absorb light and influences the gloss, hiding power, tinting strength and lightening power in case of paints. Other important uses of pigment are in varnishes, plastics, artists color, leather industries, building materials, floor coverings, rubber, paper, cosmetics, ceramics, glazes and enamels. The white lead, $\text{Pb}(\text{CO}_3)_2 \cdot \text{Pb}(\text{OH})_2$, a conventional white pigment is largely replaced by other white pigments such as TiO_2 , because of lead poisoning. White lead compounds were also used as lubricants for bearings, pottery & ceramics and in interior house coatings. The quantitative estimation of white lead to determine lead percentage using standard EDTA provides an important example of analysis of pigments.

Principle and outline:

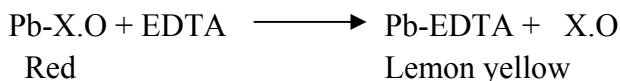
White lead is basic lead carbonate $\text{Pb}(\text{CO}_3)_2 \cdot \text{Pb}(\text{OH})_2$. When it is dissolved in acetic acid lead goes into the solution as lead acetate.



Standardisation of EDTA solution is done by titrating with a standard solution of lead nitrate using xylenol orange (X.O.) indicator at pH 6. Then concentration of pigment solution is found out by titrating with EDTA solution using the same indicator at pH 6. EDTA ($\text{Na}_2\text{H}_2\text{Y}$) reacts quantitatively with Pb^{2+} ions forming a 1:1 complex.



The acidic solution of xylenol orange indicator is lemon yellow in color and its metal complexes are intense red in color. When added into Pb^{2+} solution it forms a red colored lead-xylenol orange complex (Pb-X.O.) imparting intense red color to the solution at a pH of 6. Addition of EDTA consumes free Pb^{2+} and near the end point, when all free Pb^{2+} are consumed, further addition of EDTA consumes Pb^{2+} from Pb-xylenol orange complex liberating free indicator imparting lemon yellow color to the solution.



Thus the color changes from intense red to lemon yellow. The pH is maintained around 6 by adding hexamine.

Procedure:

(i) Standardisation of EDTA solution:

Pipette out 25 mL of the given lead nitrate solution into a conical flask then add one test tube of distilled water. Add 3-4 drops of xylenol orange indicator followed by a few drops of dilute HNO_3 till it is yellow in color. Then add hexamine powder until the color of the solution changes to intense red. Titrate the solution against EDTA solution till the color changes to lemon yellow. Repeat the titration to get concordant values.

(ii) Estimation of lead in pigment sample:

Weigh accurately about 1.5 g of white lead pigment sample and transfer into a 250 mL beaker. Add 1 ½ test tube of dilute acetic acid and warm till the pigment dissolves completely. Cool and transfer quantitatively into a 250 mL standard flask. Make up to the mark with distilled water and shake well for uniform concentration.

Pipette out 25 mL of pigment solution into a conical flask and add 1 test tube of distilled water. Add about 3-4 drops of xylenol orange indicator followed by a few drops of dilute HNO_3 till it is yellow in color. Then add hexamine powder until the color turns to intense red and titrate with EDTA till the color of the solution changes to lemon yellow. Repeat the titration to get concordant values.

Result:

Percentage of lead in the given sample of white lead pigment = _____ %

Observation and calculations:***i) Standardisation of EDTA solution:***

Concentration of given $\text{Pb}(\text{NO}_3)_2$ solution = 0.025 N

Solution taken in the burette = Given EDTA solution

Solution taken in the flask = 25 mL of $\text{Pb}(\text{NO}_3)_2$ solution

Indicator used = 3 drops of xylenol orange

End point = Change of color from red to lemon yellow

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

Agreeing value, $V_1 = \text{_____ mL}$

Strength of EDTA solution, $N_1 = \frac{25 \times 0.025 \text{ N}}{V_1}$

= _____ N

ii) Estimation of lead in white lead pigment :

Weight of weighing bottle + pigment, $W_1 = \text{_____ g}$

Weight of weighing bottle, $W_2 = \text{_____ g}$

Weight of pigment, $W = W_1 - W_2 = \text{_____ g}$

Titration of pigment solution against EDTA solution:

Solution taken in the burette = Given EDTA solution

Solution taken in the flask = 25 mL of white lead pigment solution

Indicator used = 3 drops of xylenol orange

End point = Change of color from red to lemon yellow

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

Agreeing value, $V_2 =$ _____ mL

$$\begin{aligned}
 \text{Strength of pigment solution, } N_2 &= \frac{V_2 \times N_1}{25} \\
 &= \\
 &= \text{_____} N
 \end{aligned}$$

Weight of lead in 1000 mL of solution, $W_3 = N_2 \times \text{Equivalent weight of lead}$

$$= N_2 \times 207.2 \text{ g of lead}$$

=

$$= \text{_____} \text{ g of lead}$$

Weight of lead in 250 mL of solution, $W_4 = \frac{W_3}{4}$

=

$$= \text{_____} \text{ g}$$

Percentage of lead in the sample the given sample of white lead pigment = $\frac{W_4 \times 100}{W}$

=

$$= \text{_____} \%$$

Review Questions:

1. Write two important functions of a pigment.
2. What is the indicator used in the estimation of lead in white lead pigment? What is the end point?
3. Provide four applications of pigments.
4. Give the reaction of basic lead carbonate with acetic acid
5. What is the principle of quantitative estimation of white lead pigment using standard EDTA?
6. Explain the indicator action in the volumetric analysis of white lead pigment.
