VIT

Vellore Institute of Technology

(Deemed to be University under section 3 of UGC Act, 1956)

ENGINEERING CHEMISTRY LAB SCHEDULE
FALL SEMESTER 2019-20

TABLE OF CONTENTS

Important Instructions:

- Students must keep their working table clean after completing their experiment, drop the tissue/filter papers in dust bins marked as biodegradable wastes.
- Any broken glassware must be reported to lab attender.
- After entering the experimental data in the observation note, Students should get signature from the faculty, take the picture/scan of the evaluated pages and upload it in the course page within 2-3 days from the date of experiment.
- Marks distribution for each experiment: 4 M (expt. data) + 6 M (result) = 10 M (Weightage = 6 M).

Error	Marks (for Result)
0 – 2 %	= 6 marks
>2 – 4 %	= 5 marks
>4 – 5 %	= 4 marks
>5	= 1 mark

- **Caution:** Handle the chemicals, reagents, glassware and instruments carefully.
- **Safety Goggles and Peacock Blue Lab coat are Mandatory**

Water Purification: Hardness Estimation by EDTA method and its Removal using Ion-exchange Resin

1. Introduction to Hard Water and its Classification:

Water described as “hard” contains high levels of dissolved $Ca^{2+}$and Mg^{2+}ions. Ground and surface water dissolve the Ca^{2+}/Mg^{2+} containing ores/minerals from surrounding soil and rock and are enriched with these cations.Hardness is most commonly expressed as milligrams of $CaCO_3$eq. per litre. Water containing hardness causing species at concentrations below 60 mg/lare generally considered as soft; 60–120 mg/l as moderately hard; 120–180 mg/l, as hard; and more than 180 mg/l as very hard water. Based on the type of anions association with Ca^{2+}/Mg^{2+}ions, the hardness is categorized into permanent (non-carbonate) & temporary (carbonate) hardness.

2. Problems caused by Hard Water:

Hard water can cause costly breakdowns in boilers, cooling towers and plumbing. When hard water is heated, the hardness causing salts tend to precipitate out of solution, forming a hard scale or soft sludges in pipes and surfaces, thereby completely plugging pipes and restricting flows. In boilers, the scale prevents efficient heat transfer thereby resulting in energy loss and overheating thereby paving way for serious accidents. At the domestic level, hard water lessens the effectiveness of soap by forming scums/precipitates, which adhere to human skin. Human consumption of water containing excess of Ca and Mg are associated with increased risks of osteoporosis, nephrolithiasis, colorectal cancer, hypertension, stroke, coronary artery disease, insulin resistance, diarrhea and obesity.

3. Estimation of Hard Water:

Traditionally, hardness in water is estimated by complexometric titration using sodium salt of EDTAand EBT as indicator at pH = 9-10. EBT forms an unstable wine-red colored complex with Ca^{2+}/Mg^{2+}ions, which upon titrating with EDTA, results in the breaking of EBT-Ca^{2+}/Mg^{2+} unstable bond and formation of stable EDTA-Ca^{2+}/Mg^{2+} bond. The endpoint changes from wine-red (EBT-Ca^{2+}/Mg^{2+}) to steel blue (free EBT).

4. Modern Treatment of Hard Water:

Hard water is made soft by the use of a water softener i.e., ion-exchange resins (IER) which are very small porous spherical polymeric beads, with specific functional groups (sulphonic/carboxylic acid) attached to the polymeric backbone. Therefore, the IERs carrying a negatively charged exchange site can hold a positively charged ion. When the hard water is passed through the resin beads, Ca^{2+}/Mg^{2+}ions are exchanged from the solution for hydrogen/sodium ions, which are much more soluble and does not precipitate out to form scale or sludges. Eventually, the resin beads get saturated with hardness causing ions and the exhausted beads are regenerated by using a mild acid or brine solution to flush out the Ca^{2+}/Mg^{2+}ionsretained in the resin beads.

Expt. No.: **Date:**

Experiment	**Water Purification Hardness Estimation by EDTA method and its Removal using Ion-exchange Resin**
Problem definition	Hardness of water is due to the presence of dissolved calcium and magnesium salts in water. EDTA forms stable complex with hardness causing salts and is used in the removal of scale and sludge forming impurities in industrial boilers.
Methodology	EBT indicator-Metal ion complex is weaker compared to EDTA-metal ion complex. The end point is the color change from wine red (EBT-Metal ion complex) to steel blue (free EBT indicator).
Solution	Estimation of Calcium hardness (in ppm) in the given unknown sample. Understanding the water softening using ion-exchange resins.
Student learning outcomes	Students will learn to a) perform complexometric titration b) understand the efficiency of ion-exchange resins using in water purifiers

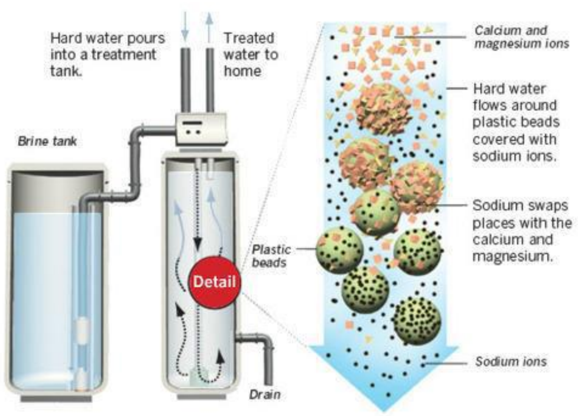
Principle:

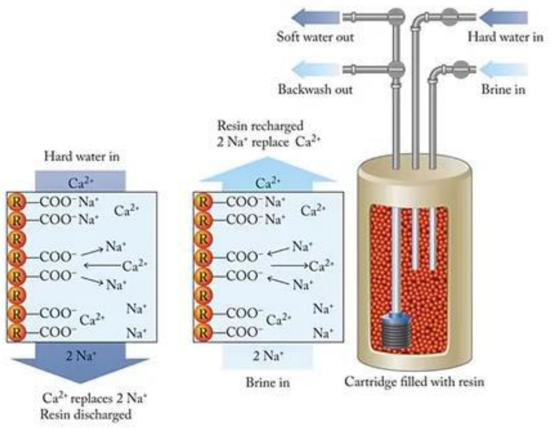
Ehtylenediaminetetraacetic acid (EDTA) forms complexes with a large number of cations including Ca^{2+} and Mg^{2+} depending upon pH of solution. Hence, it is possible to determine the total hardness of water using EDTA solution. EDTA in the form of its sodium salt (H_2Y^{2-}) is commonly used in complexometric titration for estimation of metal ion because pure EDTA (H_4Y) is sparingly soluble in water. EDTA has six binding sites (the four carboxylate groups and the two amino groups) providing six pairs of electrons. The resulting metal-ligand complex, in which EDTA forms a cage-like structure around the metal ion, is very stable at specific pH. All metal-EDTA complexes have a 1:1 stoichiometry. The H_2Y^{2-} form complexes with metal ions as follows.

$$M + H_2Y^{2-} \rightarrow MY^{2-} + 2H^+ \quad \text{-----------} \ (1)$$

Where, M is Ca^{2+} and Mg^{2+} present in water. Reaction (1) can be carried out quantitatively at pH 10 using Eriochrome Black T (EBT) as indicator. EBT forms a wine-red complex with M^{2+} ions which is relatively less stable than the M^{2+}-EDTA complex. On titration, EDTA first reacts with free M^{2+} ions and then with the metal-EBT indicator complex. The latter gives a colour change from wine-red to steel blue at the equivalence point.

Removal of hardness using ion exchange resins (IER): Ion exchange is a reversible process. When hard water is passed through cation ion-exchange resins packed in a narrow column, Ca^{2+} and Mg+ cations in hard water are exchanged with Na+ or H+ ions in the resins. The exhausted resins are regenerated by passing 10% dil. HCl through the column. A typical example of application is preparation of high-purity water for power engineering, electronic and nuclear industries and in household water purifiers.





Requirements

Reagents and solutions: Standard hard water (1mg/mL of $CaCO_3$ equivalents), 0.01 N EDTA solution, EBT indicator, hard water sample, NH_3-NH_4Cl buffer solution and ion exchange resin.

Apparatus: Burette, pipette, conical flask, standard flask burette stand and IER column.

Procedure

Titration-I: Standardization of EDTA

Pipette out 20 mL of the standard hard water containing 1mg/mL of $CaCO_3$ (1000 ppm) into a clean conical flask. Add one test tube full of ammonia buffer (NH_4OH – NH_4Cl) solution to maintain the pH around 10. Add three drops of Eriochrome Black – T (EBT) indicator and titrate it against the given EDTA solution taken in the burette. The end point is change of colour from wine red to steel blue. Repeat the titration for concordant titer values. Let 'V_1' be the volume of EDTA consumed.

S. No.	Volume of standard hard water (mL)	Burette reading (mL)		Volume of EDTA (V_1, mL)
		Initial	Final	
1				
2				
3				
			Concordant titer value	

Calculation:

20 mL of given hard water consumes V_1 mL of EDTA

20 mg of $CaCO_3$ requires V_1 mL of EDTA for complexation

$\therefore$ **1 mL of EDTA** requires = **$20/V_1$** mg $CaCO_3$ for complexation

<u>This relation will be used in other two titrations</u>

Titration-II: Estimation of total hardness of hard water sample

Pipette out 20 mL of the given sample of hard water into a clean conical flask. Add one test tube full of ammonia buffer (NH_4OH – NH_4Cl) solution and three drops of Eriochrome Black–T (EBT) indicator. Titrate this mixture against standardized EDTA solution taken in the burette. The end point is the change of color from wine red to steel blue. Repeat the titration for concordant titer value. Let 'V_2' be the volume of EDTA consumed.

S. No.	**Volume of sample hard water (mL)**	**Burette reading (mL)**		**Volume of EDTA (V_2, mL)**
		Initial	**Final**	
1				
2				
3				
			Concordant titer value	

Calculation:

From Titration 1, we have the following relation:

$\therefore$ 1 mL of EDTA requires = $20/V_1$ mg $CaCO_3$ for complexation

From Titration 2,

20 mL of sample hard water consumes = V_2 mL of EDTA.

$= V_2 \times 20/V_1$ mg of $CaCO_3$ eq.

$\therefore$1000 mL of hard water sample consumes = $V_2 \times \cancel{20}/V_1 \times 1000/\cancel{20}$

$= V_2/V_1 \times 1000$ ppm

$\therefore$ Total hardness of the water sample = "X" ppm

Titration-3: Removal of hardness using ion exchange method

Arrange the ion exchange column on to a burette stand and place a clean funnel on top of the column. Pour the hard water sample (around 40 to 50 mL) remaining after the completion of Titration – 2 through the funnel and into the ion exchange column. Place a clean beaker under the column and collect the waterpassing through the column over a period of 10minutes. Adjust the valve of the column to match the duration of outflow.

From the water collected through the column, pipette out 20 mL into a clean conical flask and repeat the EDTA titration as carried out above. Note down the volume of EDTA consumed as 'V_3'.

Calculation:

From Titration 1, we have the following relation:

$\therefore$ 1 mL of EDTA requires = $20/V_1$ mg $CaCO_3$ for complexation

From this relation, it can be seen that

20 mL of water sample after softening through the column consumes = V_3 mL of EDTA.

$= V_3 \times 20/V_1$ mg of $CaCO_3$ eq.

$\therefore$ 1000 mL of water sample after softening through the column consumes =

$= V_3 \times \cancel{20}/V_1 \times 1000/\cancel{20}$

$= V_3/V_1 \times 1000$ ppm

$\therefore$ Residual hardness of the water sample = "Y" ppm

S. No.	Volume of sample hard water (mL)	Burette reading (mL)		Volume of EDTA (V_2, mL)
		Initial	**Final**	
1				
2				
3				
			Concordant titer value	

Result:

1. Total hardness of the water sample="X" ppm
2. Residual hardness in the water sample="Y" ppm
3. Hardness removed through the column =X – Y ppm

Evaluation of Result:

Sample number	Experimental value	Actual Value	Percentage of error	**Marks awarded**

Water Quality Monitoring: Total Dissolved Oxygen Assessment in Different Water Samples by Winkler's Method

1. Importance of Dissolved Oxygen (DO): Knowledge of DO concentration in seawater is often necessary in environmental and marine sciences. It is used by oceanographers to study water masses in the ocean. It provides the marine biologist a means to measure primary production, particularly in laboratory cultures. For the marine chemist, it provides a measure of the redox potential of the water column. DO is also an important factor in corrosion. Oxygen is poorly soluble in water. The solubility of oxygen decreases with increase in concentration of the salt and hence, solubility of DO is lesser in saline water. The amount of DO at 100% saturation at sea level is 9.03 mg/L (at 20° C) and is sufficient to sustain aquatic life. Dissolved oxygen is usually determined by Winkler's method.

2. What is Winkler Method? The Winkler Method is a technique used to measure dissolved oxygen in freshwater systems. DO is used as an indicator of the water body's health, where higher DO concentrations are correlated with high productivity and little pollution. This test is performed on-site, as delays between sample collections and testing may result in an alteration in oxygen content.

3. How does the Winkler Method Work? Winkler Method uses titration to determine dissolved oxygen in the water sample. A sample bottle is filled completely with water (no air is left to skew the results). DO in the sample is then "fixed" by adding a series of reagents that form an acid compound that is then titrated with a neutralizing compound that results in a colour change. The point of colour change is called the "endpoint," which coincides with the dissolved oxygen concentration in the sample. DO analysis is best done in the field, as the sample will be less altered by atmospheric equilibration.

4. **Applications:**

Dissolved oxygen analysis can be used to determine the health or cleanliness of a lake or stream, amount and type of biomass a freshwater, the amount of DO that a system can support and the amount of decomposition occurring in the lake or stream.

Expt. No.: **Date:**

Experiment	**Water Quality Monitoring: Total Dissolved Oxygen Assessment in Different Water Samples by Winkler's Method**
Problem definition	Dissolved oxygen (DO) is essential to living organisms in water but harmful if present in boiler feed water leading to boiler corrosion.
Methodology	Winkler's titration method is used to assess DO in water.
Solution	Estimation of total dissolved oxygen in different water samples.
Student learning outcomes	Students will learn to a) perform Winkler's titration method b) assess the total dissolved oxygen in different water samples

Principle: Estimation of dissolved oxygen (DO) in water is useful in studying corrosion effect of boiler feed water and in studying water pollution. DO is usually determined by Winkler's titration method. It is based on the fact that DO oxidize potassium iodide (KI) to iodine. The liberated iodine is titrated against standard sodium thiosulphate solution using starch indicator. Since DO in water is in molecular state, as such it cannot oxidize KI. Hence, manganese hydroxide is used as an oxygen carrier to bring about the reaction between KI and Oxygen. Manganese hydroxide, in turn, is obtained by the action of NaOH on $MnSO_4$.

$$MnSO_4 + 2NaOH \longrightarrow Mn(OH)_2 + Na_2SO_4$$

$$2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2$$

$$MnO(OH)_2 + H_2SO_4 \rightarrow MnSO_4 + 2H_2O + [O]$$

$$2KI + H_2SO_4 + [O] \rightarrow K_2SO_4 + H_2O + I_2$$

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

$$\text{Starch} + I_2 \longrightarrow \text{Blue colored complex.}$$

The liberated iodine (I_2) is titrated against standard sodium thiosulphate ($Na_2S_2O_3$) solution using starch as indicator.

Requirements:

Reagents and solutions: Standard buffer of pH 7, standard potassium dichromate (0.01 N), sodium thiosulphate solution, 10% KI solution, alkali KI solution (KI + KOH in water), conc. H_2SO_4, manganese sulphate, starch solution as indicator.

Apparatus: Conical flask, Burette, Measuring flask, Beakers.

Procedure:

Titration 1: Standardization of Sodium Thiosulphate

Rinse and fill the burette with given sodium thiosulphate solution (Bottle B). Pipette out 20 mL of 0.01N $K_2Cr_2O_7$ solution (Bottle A) into a clean conical flask. To this, add 5 mL H_2SO_4 (1/2 T.T.), 10 mL of 10% KI, and titrate against sodium thiosulphate solution. When the solution becomes straw yellow colour, add starch indicator and continue the titration. End point is the disappearance of bluish brown colour. Repeat the titration to get concordant value.

Titration 2: Estimation of Dissolved Oxygen

Using a measuring cylinder, add 100 mL of sample water in a conical flask. Further, add 2 mL of $MnSO_4$ and 2 mL of alkali KI solution and shake well for the rough mixing of the reagents. Set aside the flask for few minutes to allow the precipitate to settle down and then add 2 mL of conc. H_2SO_4 for complete dissolution of the precipitate. Then, titrate against std. sodium thiosulphate solution. When the solution turn into light yellow, add starch indicator. End point is the disappearance of bluish brown colour. Repeat the titration to get the concordant value. Calculate the strength of dissolved oxygen from the titer value. Based on that, calculate the amount of dissolved oxygen in the given water sample.

OBSERVATION AND CALCULATIONS

Titration - I: Standardization of Sodium Thiosulphate

S. No.	Volume of $K_2Cr_2O_7$ (mL)	Burette reading (mL)		Volume of sodium thiosulphate (mL)
		Initial	Final	
1				
2				
3				
Concordant value				

Calculations:

Volume of potassium dichromate V_1 = 20 mL

Strength of potassium dichromate N_1 = 0.01 N

Volume of sodium thiosulphate V_2 =…………….mL (From Titration – 1)

Strength of sodium thiosulphate N_2 = ……?

$$V_1N_1 = V_2N_2$$

$$\therefore\ N_2 = V_1N_1/V_2$$

Strength of sodium thiosulphate = $N_2 = 20 \times 0.01/V_2$ =…………….. N

Titration – II: Estimation of Dissolved Oxygen

S. No.	Volume of water sample (mL)	Burette reading (mL)		Volume of sodium thiosulphate (mL)
		Initial	Final	
1				
2				
3				
Concordant value				

Calculation:

Volume of sodium thiosulphate V_2 = ……… mL (From Titration – 2)

Strength of sodium thiosulphate N_2 = ………… N (From Titration – 1 calculation)

Volume of water sample taken V_1= 100 mL

Strength of given water sample N_1 = ?

$$V_1N_1 = V_2N_2$$

$$N_1 = V_2 \text{ X } N_2/100$$

$$= \ldots\ldots\ldots\ldots\ldots \text{ N}$$

Amount of dissolved oxygen (ppm) = normality × equivalent weight of O_2 × 1000 mg/L of the given water sample.

$$= \ldots\ldots\ldots\ldots\ldots\ldots\text{N} \times 8 \times 1000 \text{ mg/L}$$

= ------------------ ppm.

Result: Amount of dissolved oxygen in the given water sample = ……… ppm.

Evaluation of Result:

Sample number	Experimental value	Actual Value	Percentage of error	**Marks awarded**

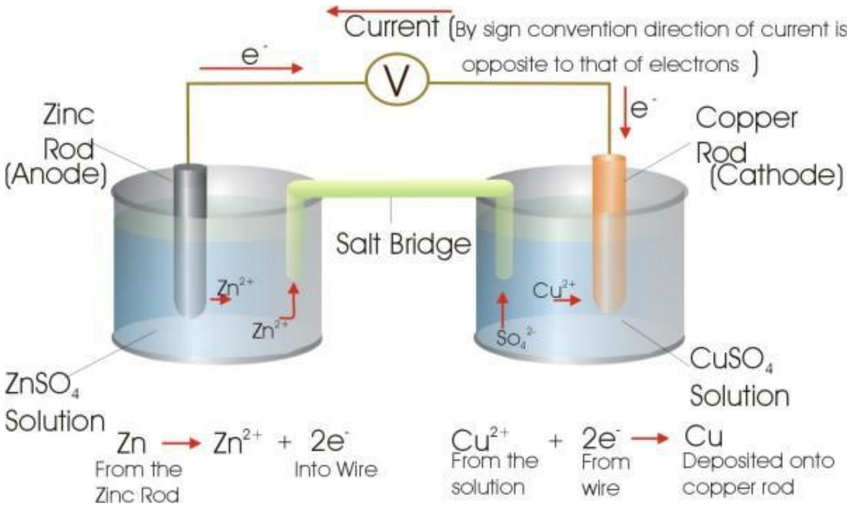
Construction and working of an electrochemical cell

An Electrochemical Cell is a device used to convert chemical energy (produced in a redox reaction) into electrical energy. Electrochemical Cells are also known as Galvanic Cells.

If we take a zinc rod and place it in a container filled with copper sulphate solution, heat will be produced. This happens due a spontaneous redox reaction given below:

$$Zn_{(Solid)} + CuSO_{4(Aqueous)} \Rightarrow ZnSO_{4(Aqueous)} + Cu_{(Solid)} \text{ deposited}$$

As the reaction would proceed, the zinc rod would get eroded and copper particles would get deposited and solution would become warm.



An Electrochemical Cell

The oxidation reaction in the zinc rod releases $2e^-$ and are taken by the Copper ion in the $CuSO_4$ solution. If these two half reactions can be separated, then the electrons can be made to move through a wire. In this manner, we can produce electrical energy from chemical energy. The salt bridge is a concentrated solution of inert electrolytes. It is required for completing the circuit. It allows the movement of ions from one solution to the other.

Applications: Electrochemical cell would be useful to be able to convert this chemical energy to electrical energy (in Battery) instead of heat energy. This process is also used in electroplating industry to coat Fe metal with Zn/Al coatings.

Expt. No.: **Date:**

Experiment	**Construction and working of an Zn-Cu electrochemical cell**
Problem definition	Measurement of electrode potential and construction of a battery system
Methodology	Single electrode potentials of Zn/Zn^{2+} and Cu/Cu^{2+} system and Daniel Cell
Solution	Electromotive force measurement (EMF) as voltage
Student learning outcomes	Students will learn to perform a) Electrode potential relevant to battery b) Understanding of a normal battery system

Principle: The electromotive force (emf) of an electrochemical cell is measured by means of a potentiometer. An electrochemical cell (E_{cell}) is considered as a combination of two individual single electrodes. The potential difference between the two single electrode potentials is a measure of emf of the cell (E_{cell}). In order to measure the potential difference between electrodes in contact with electrolyte containing the same cation, it is necessary to have another electrode in contact with electrolyte of same cation, both the half-cells connected through a salt bridge. Saturated calomel electrode (SCE; $E_{calomel}$) whose potential is known, is used as a reference electrode and it is coupled with the metal electrode for which the potential is to be determined.

Hg / Hg_2Cl_2 (s), saturated KCl ║ (N/10) electrolyte of the metal / Metal

From the emf of the cell involving saturated calomel electrode and metal electrode dipped in its solution of 0.1 N electrolyte, electrode potential of the metal electrode is readily calculated using the standard potential of calomel electrode as;

$$E_{cell} = E_{M/M^+} - E_{calomel}$$

$$E_{M/M^+} = E_{cell} + E_{calomel}$$

E_{cell} is total emf of the cell. Electrode potential of the metal electrode is given by Nernst equation as;

$$E_{M/M^+} = E^\circ + \frac{RT}{nF} \text{ In } a_M^{n+}$$

$$E^\circ_{M/M^+} = E_{M/M^+} - \frac{RT}{nF} \text{ In } a_M^{n+}$$

$$E^\circ_{M/M^+} = E_{M/M^+} - \frac{0.0595}{n} \text{ Iog } a_M^{n+}$$

Requirements:

Reagents and solutions: $CuSO_4$ stock solution (0.1N), $ZnSO_4$ stock solution (0.1N), KCl salt.

Apparatus: Digital potentiometer, copper electrode, zinc electrode, calomel electrode, 100 mL beaker, burette, 50 ml standard flasks.

Procedure:

Calibrate the digital potentiometer with the help of the wires to display 1.018 V. The metal electrode is sensitized by dipping in a small quantity of 1:1 nitric acid containing a small quantity of sodium nitrite until effervescence occurs. Then the electrode is washed well with distilled water. 50 mL of the given concentration of the electrolyte solution is taken in a beaker and its corresponding metal electrode is introduced. This is connected with the saturated calomel electrode (half-cell) by means of a salt bridge. The metal electrode is connected to the positive terminal and the calomel electrode is connected to the negative terminal of the potentiometer. EMF of the cell (E_{cell}) is measured and noted in **Table 1**. Standard electrode potential [$E°_{M/M}{}^{2+}$] is computed using Nernst equation (**Eq. 1**).

Table 1: EMF measured for various concentrations of M/M^{n+} system

Electrode/ Electrolyte	**Electrolyte conc. (N)**	**E_{cell} (V)**	**$E_{M/M+}$ = $E_{cell} + E_{calomel}$**	**$E°_{M/M}{}^{+}$ [From Eq. (1)]**	**Average $E°_{M/M}{}^{+}$**
Zn/Zn^{2+}	0.01 N				
	0.02 N				
	0.05 N				
Cu/Cu^{2+}	0.01 N				
	0.02 N				
	0.05 N				

Solution Temperature (T) = °C; Potential of SCE = 0.244 + 0.0007 (25 °C)

$$\mathbf{E°_{M/M}{}^{+} = E_{M/M}{}^{+} - \frac{0.0595}{n} \log [\gamma_c \times C]} \quad \text{------} \quad (1)$$

where, E° is standard electrode potential of metal electrode; $a_M{}^{n+}$ is activity of metal ions in solution ($a_M{}^{n+} = \gamma_c[C]$); γ_c is activity coefficient (Table 2) and C is concentration of electrolyte solution.

Table 2: Individual activity coefficients of Cu^{2+} and Zn^{2+} in water at 25 °C

Metal ion system (Cu^{2+}/Zn^{2+})	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2
Activity coefficient (γ_c)	0.905	0.870	0.809	0.749	0.675	0.570	0.485	0.405

Use this space for detailed calculation

Construction of Daniel cell and measurement of its voltage with three different concentrations of Cu/Zn solutions:

In the Daniel cell, copper and zinc electrodes are immersed in the equimolar solution of $CuSO_4$ and $ZnSO_4$ respectively.

At the anode, zinc is oxidized as per the following half-reaction: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

At the cathode, copper is reduced as per the following reaction: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

The overall reaction is: $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

Construct Daniel cell using the following concentrations of Copper and Zinc solutions and record the voltage of the cells in Table 3.

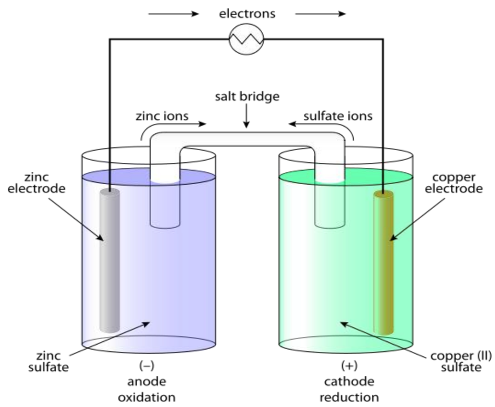


Table 3: **EMF of Daniel Cell observed from three different conc. of Zn and Cu solutions**

Metal	Concentration (N)	Metal	Concentration (N)	EMF observed (E_{cell} / V)
Zn/Zn^{2+}	0.01 N	**Cu/Cu^{2+}**	0.01 N	
	0.02 N		0.02 N	
	0.05 N		0.05 N	
			Average	

Results:

(a). Standard electrode potential of Copper (E^o) = ____________ *vs*. SCE

(b). Standard electrode potential of Zinc (E^o) = ____________ *vs*. SCE

(c). EMF of the constructed Daniel cell = __________________

Evaluation of result:

Sample No.	Experimental Value	Actual Value	Percentage of error	Marks awarded
a) $E^o_{Cu/Cu^{2+}}$				
b) $E^o_{Zn/Zn^{2+}}$				
c) EMF of Daniel cell				

Quantitative colorimetric determination of Ni^{2+} metal ions using conventional and smart phone digital-imaging methods

1. Importance of the experiment:

Nickel is a transition element and commonly exists in +2 oxidation state, though +1, +3 and +4 states are also observed in nickel complexes. Nickel plays an important role in biological systems as a constituent of several enzymes. Nickel is also present in soils and plants, and its concentration varies widely from trace quantities to being a major constituent. Therefore, determination of nickel at different concentration levels in variety of samples becomes very important.

2. Nickel Toxicity: Compared with other transition metals, Nickel is a moderately toxic element. However, it is known that inhalation of nickel and its compounds can lead to serious problems, including cancer in the respiratory system. Moreover, Nickel can cause a skin disorder known as nickel-eczema (10.1016/j.kijoms.2016.08.003).

3. Nickel in Industries: A thin layer of nickel onto a metal object can be decorative, provide corrosion resistance, wear resistance, or used to build up worn or undersized parts for salvage purposes. Nickel alloys are used extensively because of their corrosion resistance, high temperature strength and special magnetic and thermal expansion properties.

The major alloy types that are used are:

- Iron-Nickel-Chromium alloys
- Stainless Steels
- Copper-Nickel alloys and Nickel-Copper alloys
- Nickel-Chromium Alloys
- Nickel-Chromium-Iron alloys
- Low Expansion Alloys
- Magnetic Alloys (http://www.nickel-alloys.net/nickelalloys.html)

Expt. No.: **Date:**

Experiment	**Quantitative colorimetric determination of Ni^{2+} metal ions using conventional and smart phone digital-imaging methods**
Problem definition	Corrosion protection in steel depends on the amount of Ni (acts as passivating metal) in its composition. Hence, it is important to analyze the amount of Ni in steel for its use in industry.
Methodology	Ni-DMG forms a stable colored complex. With increasing concentration of Ni in solution, its color intensity also increases. In turn, the color intensity is a function of color coordinates (Red, Blue and Green, RGB) in the image taken using mobile phone camera.
Solution	Estimation of Ni concentration in the unknown sample from the calibration graph plotted based on different known Ni concentrations.
Student learning outcomes	Students will learn to perform colorimetric method, perform RGB response analysis and analyze Ni composition in different grades of steel

(i). Principle:

(a). Colorimetric method:

Photo-sensitive measurements are expressed in terms of absorbance, (A) as given in Eq. (1). Further, the linear relationship between absorbance (A) and concentration of the analyte

$$\varepsilon cl = A = \log(I_0/I) \qquad \ldots (1)$$

Where, I_0 is the incident light power, I the transmitted light power, ε = molar absorptivity, c = concentration of analyte and l = thickness of the solution.

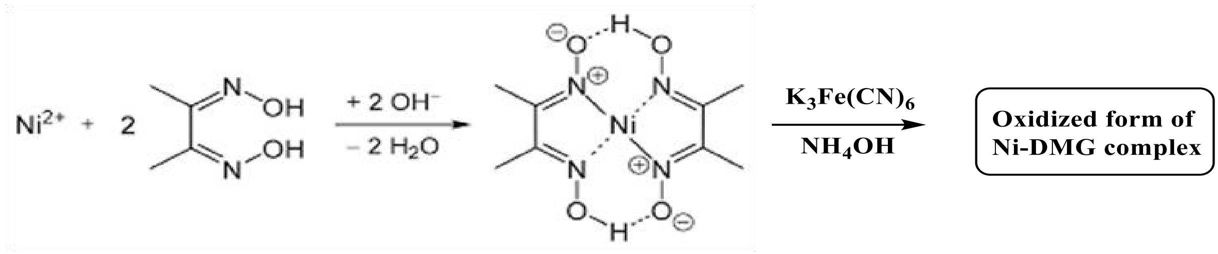
(b). Digital-imaging method:

The color and intensity of digital image are usually 24 bit data (8 bit R + 8 bit G + 8 bit B) forming an additive color space, in which R, G and B lights are added together in various combinations to reproduce a broad range of colors. By using combination of R, G and B intensities, many colors can be displayed. The intensity of each color has 256 levels (from 0 to 255). The value of R = 0, G = 0, B = 0 refers to pure black while R = 255, G = 255, B = 255 is pure white. With this system, unique combinations of R, G and B values are allowed, providing for millions of different hue, saturation and lightness shades. These extensive dynamic colors of images provide the database for quantitative analysis. The goal of this study is to employ digital images-based colorimetry for the determination of Ni^{2+} concentration in aqueous samples.

The concentration of analyte is a function of color coordinates: $c = RGB$ … (2)

(ii) Scheme of the reaction and requirements

Dimethylglyoxime (DMG) reacts with Ni^{2+} to form a pink-colored $Ni(dmg)_2$ complex in alkaline medium. It gets oxidized by potassium ferricyanide ($K_3[Fe(CN)_6]$) in alkaline medium to form a brown-red, water soluble oxidized $Ni(dmg)_2$ complex (**Scheme 1**).



Scheme - 1

Absorption spectrum of the oxidized complex shows absorption maxima at a wavelength of 440 nm (**Fig. 1**). Concentration of Ni^{2+} in the given unknown sample is determined from the calibration graph (**Fig. 2**).

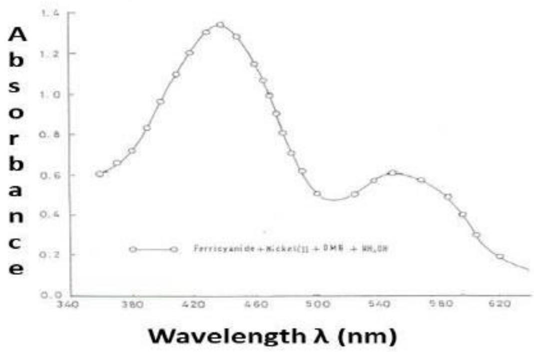


Fig. 1: Absorption spectrum of oxidized Ni(II)-DMG complex showing λ_{max} at 440 nm

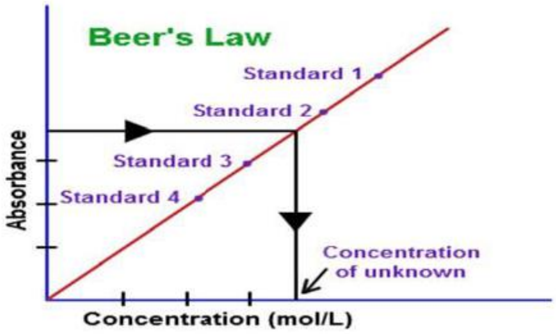


Fig. 2: Model calibration curve for Ni(II) determination

Requirements:

Reagents and solutions: $NiSO_4$ (100 ppm), NaOH (1 N) solution, DMG, $K_3[Fe(CN)_6]$

Instrument: Colorimetry and smartphone

(iii). Procedure:

(a). Colorimetry method: Take 6 standard 50 mL volumetric flasks (to prepare 5 known and 1 unknown solution). Fill the burette with Ni stock solution (100 ppm). Add 1, 2, 3, 4 and 5 mL of the Ni solution in burette to the std. flasks to get 2, 4, 6, 8 and 10 ppm of steel containing nickel(II) solutions. The unknown sample will be furnished in another 50 ml volumetric flask. Further, add 0.5 mL of DMG solution followed by 0.5 mL of $K_3[Fe(CN)_6]$ solution using a burette to all the 5 std. flasks. All the flasks are shaken well once and waited for 5 minutes. After that, make up the 50 mL mark in std. flask with 1N NaOH solution. Allow the flasks at least 10 minutes for the complete complex formation. Absorbance of the formed brown-red solution is measured at 440 nm against NaOH solution (blank). Record these absorbance readings in **Table 1**.

Draw a calibration graph taking concentration of Ni^{2+} (in ppm) as X-axis and absorbance readings as Y-axis. A straight line that passes through the origin (see **Fig. 2**) is an indication that the measured data obeys Beer's Law. From the calibration plot, measure the concentration of nickel in the given unknown sample.

(b). Digital imaging method: The prepared standard solutions are lined up along with unknown concentration sample and blank. Using a white paper as background, take a photograph of the samples by holding the camera around 50 cm away. Calibration curve will be constructed through the RGB values of analytical response with different conc. of Ni^{2+} ions using "RGB Tool" APP. In the plotted graph, RGB response varies linearly *vs* the analyte concentration. In order to get precise analysis, follow the steps given below:

Transfer prepared standard solution and unknown solution into different colorimetric test tubes

↓

Take image of all test tube solution using smart phone camera

↓

Open the image processing app

↓

Go to gallery, open the image stored in app and extract RGB values for each image/conc.

↓

Process the RGB values (R/G) or (R/B) or (G/B) etc., till to get linear response

↓

Plot the calibration curve using RGB linear response vs concentration

↓

Find the unknown conc using the calibration curve

Table 1: Experimental Data

	Data collected from Colorimetric device		Data collected from smartphone device*				
S. No.	Conc (ppm)	Abs (Y- axis)	R	G	B	G/B	B/G
1.							
2.							
3.							
4.							
5.							
	Unknown						

*If your solution looks Red or blue or green, then the corresponding ratio can be ignored and select RGB data which is linear with concentration of analyte for plotting calibration graph (Y-axis)

Result:

(i). Concentration of Ni in steel sample (using colorimetry) = ________ ppm (mg/L)

(ii). Concentration of Ni in steel sample (using digital imaging) = ________ ppm (mg/L)

Evaluation of result:

Sample number	Experimental value (ppm)	Actual value (ppm)	Percentage of error	**Least error % value**	**Marks awarded**
	Colorimetry method				
	Digital-imaging method				

Quantitative colorimetric determination of Fe^{2+} metal ions using conventional and smart phone digital-imaging methods

1. Source of Iron in drinking water: Iron is a common metallic element found in Earth crust. Water percolating through soil and rock can dissolve minerals containing iron and hold them in solution. Occasionally iron pies may also be a source of iron in water. In deep well, where oxygen content is low, the iron bearing water is clear and colourless. But that water pumped from motor is exposed to surface oxygen and change into colored solid forms, initially into white, then yellow and finally to red-brown solid precipitate that settle out of the water.

2. Iron in drinking water: Iron is one of the many minerals that are essential for human health. Without iron, people may experience anaemia, fatigue, or an increase in infections. But how much iron is too much? Drinking water that contains iron can be beneficial to your health. However, excessive iron in drinking water may have negative effects like poor skin and metallic taste in water. Because water and iron don't physically mix well, people may notice leftover soap residue after showering or bathing. This soap build-up can also cause skin problems. Iron overload can also lead to hemochromatosis - which can cause damage to the liver, heart, and pancreas. Excessive iron can leave behind a residue in plumbing lines and this is yet another reason to consider removing iron from water. There are plenty of health concerns associated with too much iron intake, which is one of the main reasons people using well water should schedule annual water testing.

3. Importance of the experiment:

Metal ions such as Fe and Ni (Lewis acid) form complex with Lewis base and show strong colours even at lower concentrations. Ideal complexing agent should be stable, selective and be free from variations in color due to minor changes in pH or temperature. Colorimetric analysis is based on the change in the intensity of the colour of a solution with variations in concentration. Colorimetric method represents the simplest form of absorption analysis. The human eye is used to compare the colour of the sample solution with a set of standards until a match is found.

http://www5.csudh.edu/oliver/che230/labmanual/iron.htm

Expt. No.: **Date:**

Experiment	**Quantitative colorimetric determination of Fe^{2+} metal ions using conventional and smart phone digital-imaging methods**
Problem definition	Excess Iron in drinking water cause negative effects like poor skin and hemochromatosis (damage to liver, heart and pancreas). There are plenty of other health concerns associated with too much iron intake, and hence it is important to estimate the amount of iron in waste samples.
Methodology	Fe and 1,10-phenanthroline forms a stable deep-red colored complex. With increasing concentration of Fe in solution, its color intensity also increases, which in turn is a function of color coordinates (Red, Blue and Green, RGB) in the image taken using mobile phone camera.
Solution	Estimation of Fe concentration in different water samples can be found out using colorimetry technique from the calibration graph plotted based on different known Fe concentrations.
Student learning outcomes	Students will learn to perform colorimetric method, perform RGB response analysis and analyze Fe composition in different grades of steel

(i). Principle:

(a). Colorimetric method:

Photo-sensitive measurements are expressed in terms of absorbance, (*A)* as given in Eq. (1). Further, the linear relationship between absorbance (A) and concentration of the analyte

$$\varepsilon cl = A = \log(I_0/I) \qquad \dots (1)$$

Where, I_0 is the incident light power, I the transmitted light power, ε = molar absorptivity, c = concentration of analyte and l = thickness of the solution.

(b). Digital-imaging method:

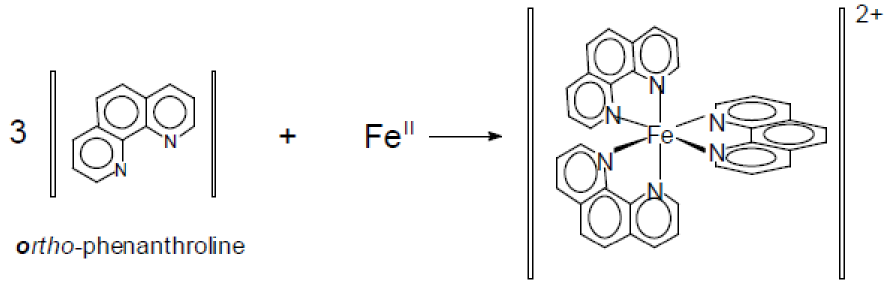
The color and intensity of digital image are usually 24 bit data (8 bit R + 8 bit G + 8 bit B) forming an additive color space, in which R, G and B lights are added together in various combinations to reproduce a broad range of colors. By using combination of R, G and B intensities, many colors can be displayed. The intensity of each color has 256 levels (from 0 to 255). The value of R = 0, G = 0, B = 0 refers to pure black while R = 255, G = 255, B = 255 is pure white. With this system, unique combinations of R, G and B values are allowed, providing for millions of different hue, saturation and lightness shades. These extensive dynamic colors of images provide the database for quantitative analysis. The goal of this study is to employ digital images-based colorimetry for the determination of Ni^{2+} concentration in aqueous samples.

The concentration of analyte is a function of color coordinates: $c = RGB \quad \dots (2)$

(ii) Scheme of the reaction and requirements

A complex of Iron (II) is formed with 1,10-phenanthroline [$Fe(C_{12}H_8N_2)_3^{2+}$] and the absorbance of this colored solution is measured with a colorimeter. Hydroxylamine (as the hydrochloride salt to increase solubility) is added to reduce any Fe^{3+} to Fe^{2+} and to maintain it in that state. The spectrum is plotted to determine the absorption maximum.

$4\ Fe^{3+}$	**$+ 2\ NH_2OH{\cdot}HCl$**	**$\rightarrow 4\ Fe^{2+}$**	**$+ N_2O$**	**$+ 4\ H^+$**	**$+ H_2O$**
Ferric Iron	Hydroxylamine Hydrochloride	Ferrous Iron	Nitrous Oxide	Proton	Water



ortho-phenanthroline

Ferrous tris-*o*-phenanthroline

Reagents and solutions: Ferrous Ammonium Sulphate (10 ppm), 1,10-phenanthroline, Hydroxylamine hydrochloride and Sodium acetate solutions

Instrument: Colorimetry and smartphone

(iii). Procedure:

(a). Colorimetry method: Take 6 standard 50 mL volumetric flasks (to prepare 5 known and 1 unknown solution). Fill the burette with Fe stock solution (10 ppm). Add 2.5, 5, 10, 15 and 20 mL of the Fe solution in burette to the std. flasks to get 0.5, 1, 2, 3 and 4 ppm of Fe(II) solutions. The unknown sample will be furnished in another 50 ml volumetric flask. Further, add 0.5 mL of hydroxyl ammonium chloride solution followed by 2.5 ml of 1,10-phenanthroline using a burette. The Fe(II)-phenanthroline complex forms at pH 2 to 9. Add 2.5 mL of sodium acetate buffer to neutralize the acid present and adjust the pH to a value at which complex forms. After that, make up the 50 mL mark in std. flask with distilled water. Allow at least 15 minutes before making absorbance measurements so that the color of the complex can fully develop. Once developed, the color is stable for hours. Obtain the absorption spectrum of the Fe solutions by measuring the absorbance from about 400 to 600 nm.

Record these absorbance readings in **Table 1**. Draw a calibration graph taking concentration of Fe^{2+} (in ppm) as X-axis and absorbance readings as Y-axis. A straight line that passes through the origin is an indication that the measured data obeys Beer's Law. From the calibration plot, measure the concentration of Iron in the given unknown sample.

Digital imaging method: The prepared standard solutions are lined up along with unknown concentration sample and blank. Using a white paper as background, take a photograph of the samples by holding the camera around 50 cm away. The calibration curve will be constructed through the RGB values of analytical response with different concentration of Fe^{2+} ions using smartphone app (RGB Tool). In the plotted graph, RGB response varies linearly *vs* the analyte concentration. In order to get precise analysis, follow the steps given below:

Transfer prepared standard solution and unknown solution into different colorimetric test tubes

↓

Take image of all test tube solution using smart phone camera

↓

Open the image processing app

↓

Go to gallery, open the image stored in app and extract RGB values for each image/conc.

↓

Process the RGB values (R/G) or (R/B) or (G/B) etc., till to get linear response

↓

Plot the calibration curve using RGB linear response vs concentration

↓

Find the unknown conc using the calibration curve

Table 1: Experimental Data

	Data collected from Colorimetric device		Data collected from smartphone device*				
S. No.	Conc (ppm)	Abs (Y-axis)	R	G	B	G/B	B/G
1.							
2.							
3.							
4.							
5.							
	Unknown						

*If your solution looks Red or blue or green then the corresponding ratio can be ignored and select RGB data which is linear with concentration of analyte for plotting calibration graph (Y-axis)

Result:

(i). Concentration of Fe in steel sample (using colorimetry) = _________ ppm (mg/L)

(i)i. Concentration of Fe in steel sample (using digital imaging) = _________ ppm (mg/L)

Evaluation of Result:

Sample number	Experimental value	Actual value	Percentage of error	**Least error % value**	**Marks awarded**
	Colorimetry method				
	Digital-imaging method				

Polymer Characterization: Determination of Viscosity of Different Natural Polymer/Synthetic Polymers

1. Importance of the experiment: Molecular weight of a polymer can be determined by different techniques such as GPC, MALDI-TOF MS, etc. Determination of polymer molecular weight through intrinsic viscosity using Ostwald viscometer is an absolute technique and is also a cost-effective method. Viscosity is the measure of resistance of a fluid to flow. Water has a viscosity of 1 cps (centipoise) at room temperature (25 ^oC) and is considered as a standard.

2. Concept: Molecular weight of polymer (M) can be derived from intrinsic viscosity data of a polymer solution. But one pre-requirement to determine the molecular weight of a polymer is the knowledge of Mark-Houwink (M-H) coefficients. Upon substitution of intrinsic viscosity and these coefficients in M-H equation, one can find out molecular weight of the polymer. M-H equation $[\eta] = KM_v^{\alpha}$, where K and α are M-H coefficients and $[\eta]$ = intrinsic viscosity of the polymer solution. In this experiment, we focus on the determination of intrinsic viscosity of the given polymer solution.

3. Applications: Nowadays, polymers have become essential requirements in our day to day activities. The end applications of the polymer depend upon its characteristics such as molecular weight, polydispersity index, thermal stability, crystalline/amorphous nature, stereochemistry, etc. Among these, molecular weight of the polymer is very important. LDPE (low density polyethylene) is used as packing materials and carry bags, whereas UHMWPE (ultra-high molecular weight polyethylene) is used as containers, tubing and other heavy-duty equipments due to its high abrasion resistance, high impact strength and low coefficient of friction. Most of the bottles for carbonated drinks, mineral water, edible oil and personal care products are made of poly(ethylene terephthalate), PET and their intrinsic viscosity values range from 0.7-0.85 dL/g, depending on the length of the polymer chain (the longer the polymer chains, the more entanglements between the chains and therefore the higher the viscosity).

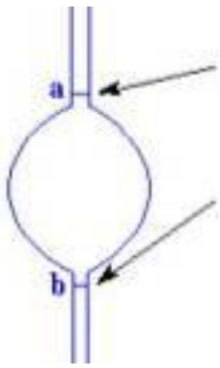


Fig. 1: A portion of Ostwald viscometer showing the upper and lower graduation marks, 'a' and 'b' respectively.

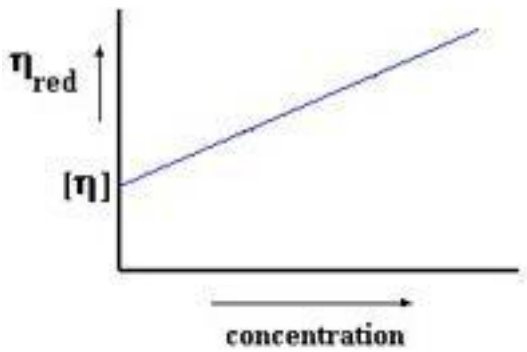
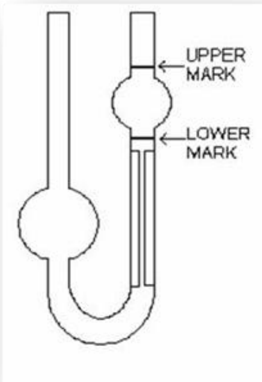


Fig. 2: A plot of reduced viscosity vs. concentration of a polymer solution, y-intercept corresponding to intrinsic viscosity$[\eta]$.

Expt. No.: **Date:**

Experiment	**Polymer Characterization: Determination of Viscosity of Different Natural Polymer/Synthetic Polymers**
Problem definition	Viscosity is the measure of resistance of a fluid to flow. Longer the polymer chains, the more entanglements between the chains and therefore the higher the viscosity. Molecular weight of polymer (M) can be derived from intrinsic viscosity data of a polymer solution.
Methodology	Determination of intrinsic viscosity using Ostwald viscometer. In a particular solvent, concentration of the polymer is directly proportional to viscosity of the solution.
Solution	Determination of intrinsic viscosity and molecular weight of the given polymer sample.
Student learning outcomes	Students will learn to determine intrinsic viscosity and molecular weight of the given polymer solution.

Principle:
When a polymer is mixed with a solvent, the solvent enters into the polymer matrix and swelling of polymer coils takes place. This expanded polymer coil disintegrates and moves out of polymer matrix and dissolves in the solvent. The apparent volume occupied by the expanded coil is referred to as the `hydrodynamic volume' of the polymer molecule in the solution under flow. Viscosity of a polymer solution is a direct measure of hydrodynamic volume of the polymer, which in turn, is a measure of its molecular weight. Viscosity of a polymer is more in a good solvent than in a poor solvent.



Reagents: PEG (polyethylene glycol) solution of different concentrations, Distilled water.

Apparatus: Ostwald viscometer, stop-clock, 50 mL standard flasks

Procedure:
Prepare at least 3 different diluted concentrations of PEG (1 to 5%) in water using 10% PEG stock solution (10 g/100 mL). Initially, rinse the Ostwald viscometer with a little amount of water. Fill it with 20 mL pure water and use a rubber filler to suck the water above the upper mark. By keeping the upper mark of the small reservoir of viscometer parallel to eyes, allow the solvent to flow down to the lower mark and note down time in seconds. This is known as the E_{flux} time. Repeat the same experiment for 2 times to get the average E_{flux} time for water (t_0). Apply the same procedure to determine the flow rate for remaining 2 diluted solutions and note down their flow time in seconds. Calculate relative viscosity, specific viscosity and reduced viscosity as shown in **Table 1.** Plot the graph between polymer concentrations (C g/mL) *vs* η_{red}. The value of intercept at C = 0 will give intrinsic viscosity of the polymer solution (see **Fig. 1**).

Table 1: Viscosity measurement data

S. No.	Concentration, C (g/mL)	E_{flux} time, t (sec)			$\eta_r = t_s/t_0$	$\eta_{sp} = \eta_r - 1$	$\eta_{red} = \eta_{sp}/c$
		t_1	t_2	$t_s = t_1 + t_2 / 2$			
1							
2							
3							

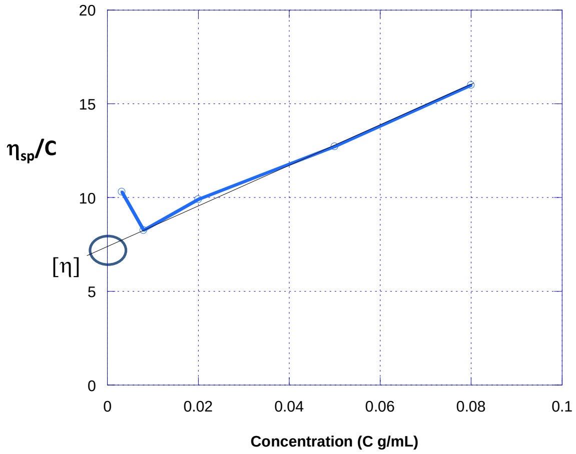


Fig. 1. Concentration (C g/mL) Vs η_{sp}/C

Calculations:

$$[\eta] = KM_v^{\alpha}$$

$\therefore$ Molecular weight of the given polymer (M_v) =

$$M = \text{Anti ln} \frac{\ln[\eta] - \ln K}{a}$$

Constants for PEG in water K = 0.0428 and a = 0.64

Result:

(a) E_{flux} time for pure water (t_0) = ________sec.

(b) Intrinsic viscosity of the polymer (η) = ---------

(c) Molecular weight of the given polymer (M_v) = ---------

Evaluation of Result:

Sample number	Skill value M_v	Calculated M_v	Error %	**Marks awarded**

Estimation of sulphate in drinking water by conductivity method

Sulphate (SO_4^{2-}) is found in almost all natural water. Origin of most sulphate compounds is the oxidation of sulphite ores, presence of shales or the industrial wastes. Ground water moving through soil and rocks containing sulphate minerals result in higher dissolved sulphate ions than permissible limit.

Problems due to excess sulphate ion concentration in water:

- Sulphates cause scale formation in boilers, pipes, etc.
- High sulphate concentration will leads to corrosion on copper piping.
- Sulphate has a laxative effect and creates diarrhoea leading to dehydration in humans and animals.
- High sulphate concentration leads to eutrophication of water bodies leads to reduction of dissolved oxygen Sulphate will give bitter taste to water if the concentration exceeds beyond 250 ppm.

Methods to estimate sulphate ion concentration in water:

1. **Turbidimetry method:** It involves the measurement of turbidity formed when an aliquot of $BaCl_2$-gelatin reagent is added to acidified sulphate solution.
2. **Titrimetric method**: By dissolving precipitated $BaSO_4$ in excess of EDTA solution and the excess EDTA is back titrated with standard Zinc solution.
3. **Colorimetric Measurement:** Based on the reaction of barium chloranilate with sulphate ion at pH 4 in ethanol yield highly coloured acid-chloranilate ion and is measured at 530 nm.
4. **Conductometric method:** This method measures the conductivity of the solution as the titration proceeds. Conductance tends to vary with the characteristics of the solvent, number, size and charge of ions involved. When one ion is replaced by another ion significantly during the titration, conductance will change in a linear manner until the replacement is complete. After that, the line will change to different slope due to the additional inclusion of another ion of difference conductance.

Expt. No.: **Date:**

Experiment	**Estimation of sulphate in drinking water by conductivity method**
Problem definition	People using water with high levels of sulfate are vulnerable to dehydration and diarrhea. Kids are more sensitive to sulfate than adults.
Methodology	Conductivity of the soluble sulphate solution will change when it is precipitated by $BaCl_2$. Conductivity will reach minima when all sulphate ions are precipitated, and from which, the total amount of sulphate ion present in the water can be determined.
Solution	Amount of $BaCl_2$ required to remove the dissolved sulphate can be estimated.
Student learning outcomes	Students will learn to a) perform conductometric method b) remove sulphate ion from irrigate water

Principle:

Electrolyte solutions conduct electricity due to the presence of ions in solution. In case of precipitation titration between $BaCl_2$ and Na_2SO_4, the conductance decreases slowly due to the replacement of Cl^- ion by SO_4^{2-} ion upto the equivalence point. After the equivalence point, the conductance increases rapidly due to the excess addition of $BaCl_2$ which remains in solution as Ba^{2+} and Cl^-. This makes detection of neutralization point easy from the conductance trend plotted as a graph. This is the principle used in the estimation of SO_4^{2-} from contaminated water sample.

Requirements:

Reagents and solutions: $BaCl_2$ (0.1 N), Na_2SO_4 (0.02 N), unknown sulphate solution and distilled water.

Apparatus: Conductivity Bridge, Conductivity cell, Burette, Pipette, Volumetric flasks, Glass rod, Beaker (100 mL).

Procedure:

Calibration of Conductivity meter: Place a freshly prepared 0.1 N KCl solution (given in bottle) in a 100 mL beaker. Dip the conductivity cell in this solution and connect to the Conductivity meter. Press “CAL” button and complete the internal calibration of the instrument.

Standardization of $BaCl_2$ (Titration – 1):

Pipette out 20 mL of 0.02 N Na_2SO_4 solution (from Bottle A) in a 100 mL beaker and add 10 mL of distilled water to it to make the conductivity cell dip completely in the solution. Addition of water will not affect the conductivity since the number of ions in the solution remains unaltered. Dip the conductivity cell into the solution in the beaker and connect to the conductivity meter. Fill the burette with ~0.1 N $BaCl_2$ solution (from Bottle B). Record the conductivity of the sulphate solution without adding any $BaCl_2$ from the burette (0^{th} reading). Add 1 mL $BaCl_2$ of known concentration into the beaker, stir with glass rod and note down the conductance. Continue the addition of $BaCl_2$ (1 mL each time) and note the conductance after each addition. Continue the titration beyond the equivalence point for about 5 mL. The conductance will either decrease slightly or remain constant until complete precipitation of $BaSO_4$, and then starts increasing on continuing the addition of $BaCl_2$. A graph is now drawn by plotting conductance *vs* volume of $BaCl_2$ added. Intersection point from the plot gives the volume of $BaCl_2$ required for precipitating the sulphate present in the known sample.

Estimation of unknown sulphate in the given solution (Titration – 2):

Make up the unknown sulphate solution given in a 100 mL standard flask upto the mark using distilled water resulting in a solution containing 0.96 mg/mL of sulphate ions (Eq. wt. of SO_4^{2-} = 48.03). Pipette out 20 mL of this solution into a 100 mL beaker and add 10 mL distilled water to it. Dip the conductivity cell and repeat the above procedure with the unknown sulphate solution to determine the amount of $BaCl_2$ required for precipitating the unknown sulphate in the sample.

From the two titrations carried out, calculate the amount of sulphate present in the effluent sample.

Table 1: Conductometric Titrations

Titration-1: Standardization of $BaCl_2$		**Titration-2: Estimation of sulphate content**	
Burette: $BaCl_2$ solution (~0.1 N) Beaker: 20 mL of Na_2SO_4 (0.02 N) + 10 mL of distilled water Conductivity cell, Conductivity meter		Burette: std. $BaCl_2$ solution Beaker: 20 mL of unknown sulphate solution + 10 mL of distilled water Conductivity cell, Conductivity meter	
Volume of $BaCl_2$ added (mL)	Conductance (μ mhos)	Volume of $BaCl_2$ added (mL)	Conductance (μ mhos)
0.0		0.0	
1.0		1.0	
2.0		2.0	
3.0		3.0	
4.0		4.0	
5.0		5.0	
6.0		6.0	
7.0		7.0	
8.0		8.0	
9.0		9.0	
10.0		10.0	
11.0		11.0	
12.0		12.0	

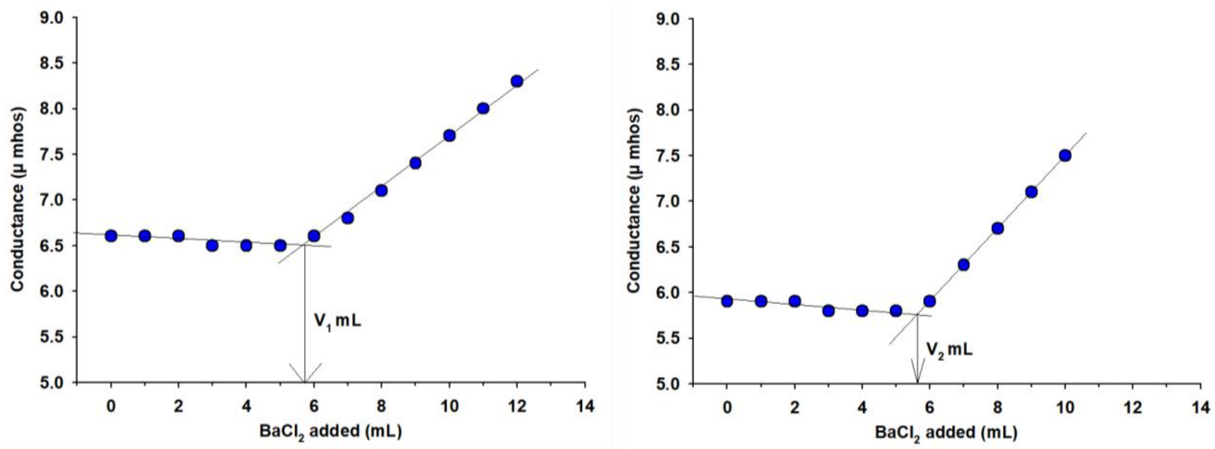


Fig 1: Model graphs – 1 and 2 for Conductometric estimation of known and unknown sulphate sample solutions, respectively.

Calculations:

A). Standardization of 0.1 N $BaCl_2$:

(N x V) of $BaCl_2$ solution = (N x V) of sodium sulphate

N of $BaCl_2$ solution = $\frac{0.02 \text{ N x } 20 \text{ mL}}{\text{Volume measured from Plot-1 } (V_1)}$

= ________ N of $BaCl_2$ solution

B). Estimation of unknown sulphate:

(N x V) of irrigation water sample = (N x V) of $BaCl_2$ solution

N of irrigation water sample = $\frac{\text{N of } BaCl_2 \text{ x Volume measured from Plot-2 } (V_2)}{20 \text{ mL}}$

= ________ N of irrigation water sample

Amount of sulphate present in 1L = Normality of irrigation water sample x Eq. wt. of SO_4^{2-} (48.03)

Amount of sulphate present in given sample solution = $\frac{\text{Strength of irrigation water sample x 48.03 x100}}{1000}$

= __________ grams in 100 mL

Result: Amount of sulphate in given irrigation water sample =_________ grams.

Evaluation of Result:

Sample number	Experimental value	Actual Value	Percentage of error	**Marks awarded**

Iron in carbon steel by potentiometry

1. Importance of the experiment: Steel production is an index of national prosperity and economy, and is globally used in variety of industrial sectors like shipbuilding, automobiles, construction, machinery and tools. Carbon steel is one variety in which nearly 96% of iron is alloyed with nearly 2% of carbon and other elements like manganese, chromium, nickel and copper. The composition is varied for achieving desired strength, ductile and long-term wearing properties. Thus, qualitative determination of iron in steel is very important.

2. Concept: Potentiometric titration is a process of determining the quantity of a sample by adding measured increments of a titrant until the end-point. The potential difference between indicator and reference electrodes is measured under conditions where the current passed is sufficiently small to maintain thermodynamic equilibrium. Potentiometric titrations provide reliable data than conventional titrations with chemical indicators especially with coloured or turbid solutions. In this experiment, Fe^{2+} is oxidised to Fe^{3+} by $KMnO_4$ as a redox titration.

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

Change in the concentration of Fe^{2+} ions during the addition of $KMnO_4$ is monitored by measuring the solution potential which is the basis for this experiment. From Nernst equation, a measurable quantity - voltage or potential is related to the concentration of species (Fe^{3+}/Fe^{2+}) in the solution.

$$E = E_0 + \frac{RT}{nF}\ln\left(\frac{Fe^{3+}}{Fe^{2+}}\right)$$

At the end point, a rapid change in the potential would be observed indicative of the complete conversion of Fe^{2+} to Fe^{3+}. A plot of observed potential vs volume of $KMnO_4$ consumed or its first derivative graph ($\Delta E/\Delta V$ *vs* average volume of $KMnO_4$) is used to detect the titration end point, which in turn, is used to qualitatively measure the amount of Fe^{2+}.

3. Applications: Potentiometry method is an electroanalytical technique which can be used to determine accurately the iron content in steel samples for industrial applications without using any indicator. This method is also useful for dilute or unknown samples or compositions for which identification of appropriate chemical indicators are challenging.

Expt. No.: **Date:**

Experiment	**Iron in carbon steel by potentiometry**
Problem definition	Mechanical properties of steel depend on its composition. Hence, it is important to analyze the amount of Iron in steel for industrial applications.
Methodology	Potentiometric method using $KMnO_4$ (oxidizing agent) to oxidize Fe(II) in steel to Fe(III) facilitates the estimation of Iron in steel.
Solution	Estimation of iron (%) in different steel samples.
Student learning outcomes	Students will learn to a) perform potentiometric method b) analyze the composition of iron in different grades of steel

Principle:

Potassium permanganate ($KMnO_4$) oxidizes ferrous ion to ferric ion in the presence of acid as per the reaction:

$$5Fe^{+2} \rightarrow 5Fe^{+3} + 5e^{-} \text{ ....(1)}$$

$$MnO_4^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_2O \text{ ....(2)}$$

$$\text{Overall, } \mathbf{5Fe^{+2} + MnO_4^{-} + 8H^{+} \rightarrow 5Fe^{+3} + Mn^{2+} + 4H_2O}$$

Electrode potential (oxidation potential) in the titration depends upon the concentration of Fe^{2+}, Fe^{3+} and H^{+} ions. To avoid the effect of the change in H^{+} ion concentration, the titration is usually carried out in large excess of acid. Oxidation potential of this redox system is given by

$$E = E_0 + \frac{RT}{nF}\ln(\frac{Fe^{3+}}{Fe^{2+}})$$

Connecting the redox electrode (Platinum) with a saturated calomel electrode (SCE) completes the necessary cell as indicated below:

$$\mathbf{Hg \,|\, Hg_2Cl_2\,(s), Saturated\ KCl \;||\; Fe^{3+}, Fe^{2+} \,|\, Pt}$$

When $KMnO_4$ is added, Fe^{2+} is oxidized to Fe^{3+} whose concentration increases with progressive addition of $KMnO_4$. The observed EMF gradually increases. At the end point, there will be a sharp increase due to the sudden removal of all Fe^{2+} ions. Plot-1: EMF measured (E) *vs* Volume of $KMnO_4$ added and Plot-2: $\Delta E/\Delta V$ *vs* Average volume of $KMnO_4$ was drawn. End point of the titration is measured from the Plot-2 graph.

Requirements:

Reagents and solutions: 100 mL of $KMnO_4$ (0.05 N) solution, 100 mL of steel solution, 2 N H_2SO_4.

Apparatus: Calomel electrode, Platinum electrode, Potentiometer, Volumetric flasks, Burette, Pipette, Beakers.

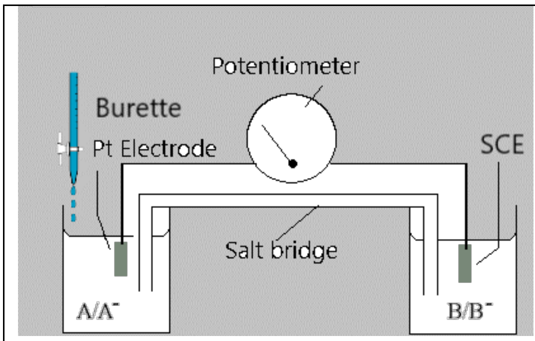


Fig. 1: Typical apparatus for potentiometric titrations.

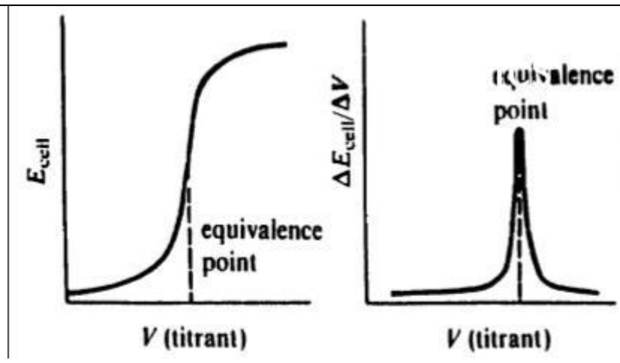


Fig. 2: Typical Potentiometric titration curves. (a) Normal curve and (b) First derivative curve.

Procedure:

Calibration of Potentiometer: Switch on the potentiometer and connect the standard cell terminals to either channel A (move channel switch to position A) or channel B (move the channel switch to position B). The meter should read 1.018 V. In case it is not 1.018 V, adjust the std. knob to obtain reference value.

Estimation of Fe(II) in steel: Transfer the given unknown steel [containing Fe(II)] solution into a clean 100 mL standard flask and make the solution up to the mark with distilled water and mix well. Pipette out 20 mL made up steel sample solution into a clean 100 mL beaker and add one test tube of dil. H_2SO_4 (2 N). Place Pt electrode in the beaker and connect to the +ve terminal of the potentiometer. In another beaker, place 50 mL of saturated KCl solution and dip the SCE in the solution and connect to the -ve terminal of the potentiometer. Place a salt bridge to complete the cell. Read the EMF of the cell and note down the value. Add 1 mL of $KMnO_4$ solution from the burette to the beaker containing steel sample solution. Stir the solution carefully and measure the EMF. Continue the addition of $KMnO_4$ solution and record the EMF for every 1 mL addition as per procedure till the potential shows a tendency to increase rapidly. After the abrupt change in cell EMF is observed, continue the titration to take 5 more reading by adding 1 mL burette solution every time. Plot EMF (ordinate) *vs.* volume of $KMnO_4$ added (abscissa) to get S-shaped curve which indicate the volume range of the end point.

To find out the volume of end point more precisely, carry out the 2nd titration in similar way but by adding 1 mL aliquots of $KMnO_4$ initially and then 0.1 mL aliquots between the two volumes where the end point is detected. Continue the titration beyond the end point as done above. The exact end point is determined by differential method i.e. by plotting $\Delta E/\Delta V$ *vs* average volume of $KMnO_4$ added. Calculate the normality strength of the Fe(II) in the given solution.

OBSERVATION AND CALCULATIONS

<u>Potentiometric Titration-I:</u>

Burette: $KMnO_4$ solution (0.05 N)

Beaker: 20 mL of steel solution containing Fe(II) + 20 mL (one test tube) of dil. H_2SO_4

Electrodes: Indicator electrode (Pt) to red terminal and SCE to black terminal

S. No.	Volume of $KMnO_4$ (mL)	EMF (volts)	S. No.	Volume of $KMnO_4$ (mL)	EMF (volts)
1			11		
2			12		
3			13		
4			14		
5			15		
6			16		
7			17		
8			18		
9			19		
10			20		

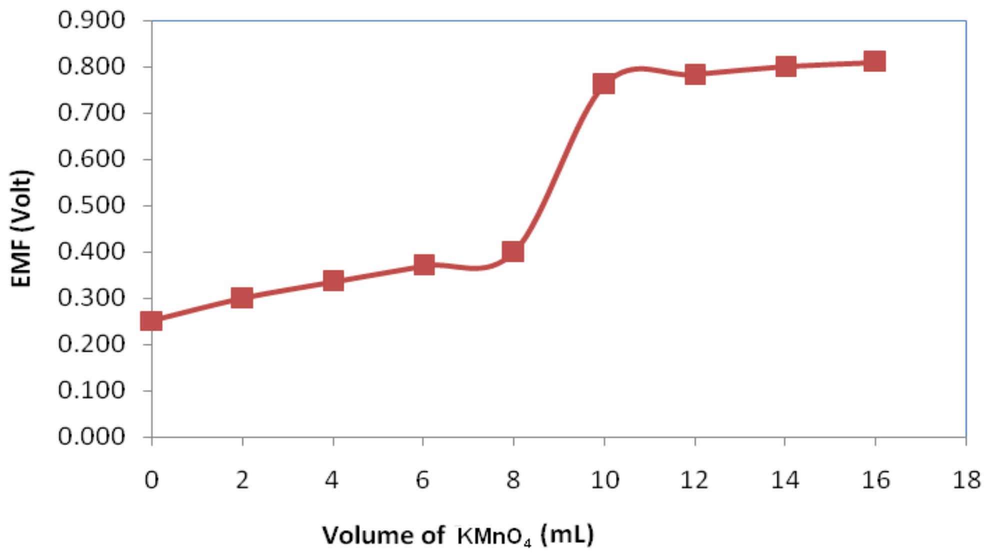


Fig. 3: Plot of EMF *vs* Volume of $KMnO_4$ added (mL)

Potentiometric Titration-II:

Burette: $KMnO_4$ solution (0.05 N)

Beaker: 20 mL of steel solution containing Fe(II) + 20 mL (one test tube) of dil. H_2SO_4

Electrodes: Indicator electrode (Pt) to red terminal and SCE to black terminal

Sl. No.	**Vol. of $KMnO_4$ (mL)**	**EMF (Volt)**	**ΔE (Volt)**	**ΔV (mL)**	**ΔE/ΔV (Volt/mL)**	**Average Volume (mL)**
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						

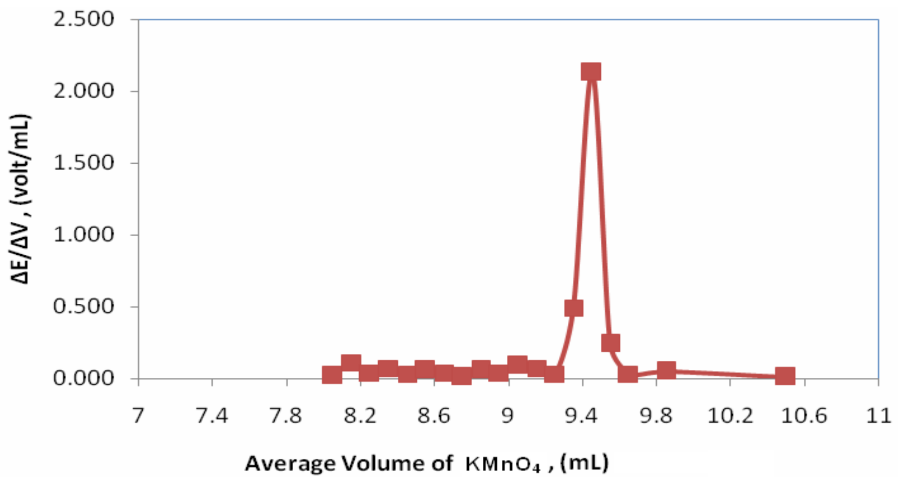


Fig. 4: Plot of ΔE/ΔV *vs* Average volume of $KMnO_4$ added.

Calculation:

$$(N \times V) \text{ of steel sample solution} = (N \times V) \text{ of } KMnO_4$$

$$N \text{ of steel sample solution} = \frac{0.05\ N \times \text{Volume of } KMnO_4 \text{ from Plot-2}}{20\ mL \text{ of steel sample}}$$

= ____________N

Amount of Fe present in 1L of sample solution = Normality of steel sample x Atomic weight of Fe (55.85)

$$\text{Amount of Fe present in given sample solution} = \frac{\text{Normality of steel sample} \times 55.85 \times 100}{1000}$$

=_______________grams in 100 mL

Result: The amount of Iron present in given steel sample is found to be =_________ grams.

Evaluation of Result:

Sample number	Experimental value	Actual Value	Percentage of error	**Marks awarded**

Expt. No.: **Date:**

Experiment	**Demo experiment: Monitoring pH/temperature/conductivity of industrial water samples using Arduino microcontroller based sensor/conventional microcontroller based systems**
Problem definition	A strong acid like HCl titrated against weak base like Na_2CO_3 results in a pH change which can be monitored using a conventional pH meter.
Methodology	Conventional microcontroller based pH meter can be replaced with an Arduino board to acquire and process the data obtained from the pH probe, and the data can be stored/transmitted for further analysis.
Solution	Monitoring of pH using Arduino microcontroller based sensor.
Student learning outcomes	Students will understand the real-time monitoring of acid-base titration using Arduino microcontroller based sensor

Introduction:

In this demo, students will be able to understand the real-time monitoring of acid-base titration using Arduino microcontroller based sensor. Acid-base titration is a common lab experiment and finds its application is wide variety of problems. A strong acid (HCl) is titrated against weak base (Na_2CO_3) and the change in pH is monitored using a pH meter. When the pH reaches 7, it indicates the end point. Instead of using a conventional microcontroller based pH meter, we can use an Arduino board to acquire and process the data obtained from the pH probe. Arduino is an open source electronics board, finding its application in all the domains of S&T. Arduino board is programmable and can be connected to laptop or smart phone (using Bluetooth) to get the data.

Experiment:

When acid is titrated with base, there will be change in pH of the resulting solution. The pH probe will measure the pH and will give the output as voltage. This voltage is then feed into the Arduino board as analog input and can be stored in the computer.

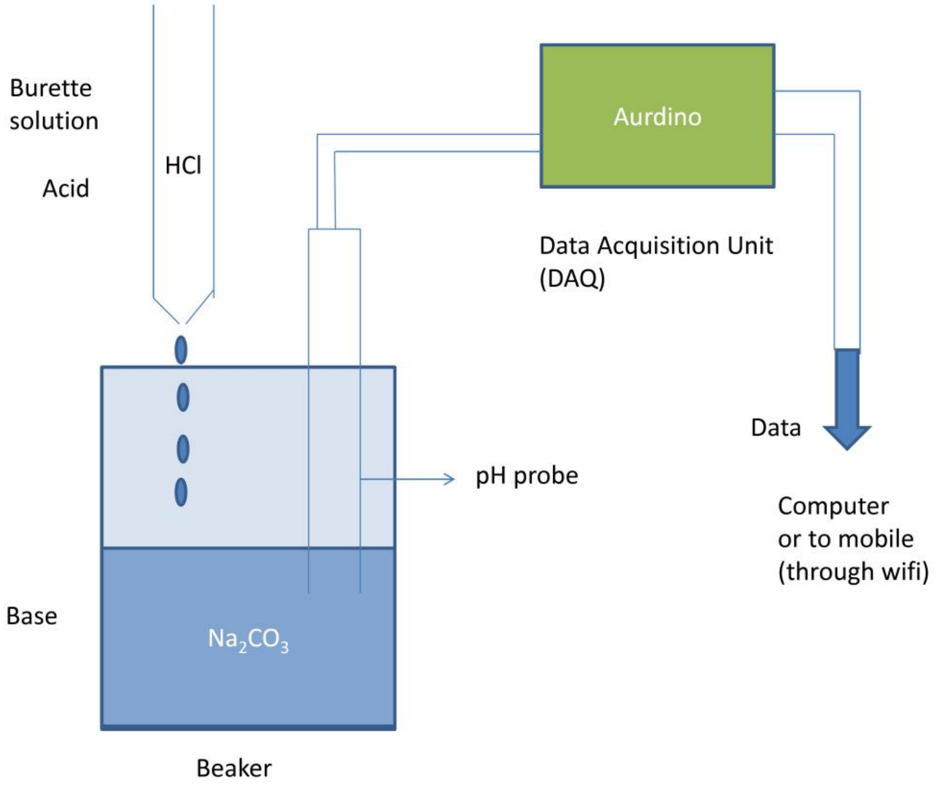


Fig. 1: Pictorial representation of the experimental setup

Course outcome:

After the end of this demo experiment, the students can

1) Learn chemistry behind acid acid-base titration.
2) Measure pH of any solution.
3) Can use and program Arduino board and apply it to measure and control any other property or devices respectively.
4) Acquire the knowledge of electronics, data acquisition and processing.
5) Understand the technology behind the measurement and instrumentation.
6) Since the Arduino is programmable, the student has flexibility to alter the experiment and can customize it for different applications.

Real setup with pH probe and Arduino: [Ref: https://www.sparkyswidgets.com/portfolio-item/ph-probe-interface/]