Laboratory Manual

Applied Chemistry (UCB008)

School of Chemistry & Biochemistry
Thapar Institute of Engineering &Technology
(Deemed to be University) Patiala - 147004

Preface

A Brief Overview of the Applied Chemistry (UCB008) Course & Online Laboratory Manual

Course Objective: The course aims at elucidating principles of applied chemistry in industrial systems, water treatment, engineering materials and analytical techniques.

Applied Chemistry (UCB008) is a **4.5 credits** course which comprises lectures, tutorials and practicals. Typically, there are 3 lectures (of 1 hour each), 1 tutorial (1 hour) and 1 practical (2 hours) per week (i.e., L T P **Cr** = 3 1 2 **4.5**). Attending all of the classes is mandatory and the attendance should be maintained at ≥75% (combined number of hours of L, T and P).

The "Practicals" are conducted in the Chemistry laboratories (designated as 'CBOL' and 'CBCL'; located on the ground floor of 'G'-block) at the School of Chemistry and Biochemistry (SCBC), Thapar University, which gives students an opportunity to carry out experiments related to important chemical concepts that they have learnt during the course. During practical's, the students are exposed to various instruments, experimental techniques, and laboratory safety practices. Students are expected to perform 11 experiments and are evaluated for practical examination just before the start of end semester examination.

The **Online Lab Manual** serves as an important source of information for the Applied Chemistry Practicals. The manual consists of detailed information on writing and maintaining a good laboratory notebook, experimental procedure, theories, chemical structures, and safety precautions required for each experiment. The students are required to go through each of the experiment and its related information.

Outcome of practical's and the list of the experiments to be performed

Laboratory Work Outcome: Students will perform experiments involving the use of pH meter, conductivity meter, potentiometer and colorimeter. They will also learn to determine the hardness, alkalinity, chloride, chromium, iron, and copper content in aqueous medium. The 'Practical' component of this course consists of 12 experiments that can be broadly classified into two types:

I. Volumetric Analysis-based
II. Equipment/Instrument-based

Following is a list of experiments in both the categories:

I. Volumetric Analysis-based Experiments

1. To determine the amount of NaOH and Na_2CO_3 present in the same solution.
2. To find the temporary and permanent hardness of water sample by complexometric titration using standard EDTA solution.
3. To determine the copper content of a given sample solution of copper ore using 0.1 N sodium thiosulphate solution iodometrically.
4. To estimate the available chlorine in bleaching powder.
5. To determine the amount of Fe^{+2} and Fe^{+3} ions by permanganometry.
6. To find out the total alkalinity and sulphate content in a water sample.

II. Equipment/Instrument-based Experiments

1. To determine the strength of given sodium hydroxide solution by titration with standard hydrochloric acid conductometrically.
2. Determine pK_a value of acetic acid by pH-metric titration.
3. Spectrophotometric determination of Fe^{2+} with 1,10-phenanthroline.
4. To titrate potentiometrically FAS solution against potassium permanganate and to determine the standard electrode potential of Fe^{2+} / Fe^{3+} system.
5. To determine the total cation concentration in natural water.
6. Determination of cloud and pour point of given oil sample (Demonstration only).

Maintaining a Laboratory Notebook: Tips on Writing, Preparing Graphs etc.

Keeping a laboratory notebook, which serves as a permanent record, is an extremely important part of Science and Engineering curriculum and gives detailed information about the objective, procedure, observations, calculations and result of an experiment that is carried out. Please ensure that the **writing is complete, thorough, and legible**.

❖ Organization of a good lab notebook

Conventionally, a chemistry laboratory notebook comprises two kinds of pages namely, a 'blank page' and a 'ruled page' that are adjacent to each other wherein experimental details are filled. In addition to these, a title page and an index page are also present at the beginning of the notebook. Following are the universally acknowledged rules of writing and maintaining a good, comprehensive laboratory notebook:

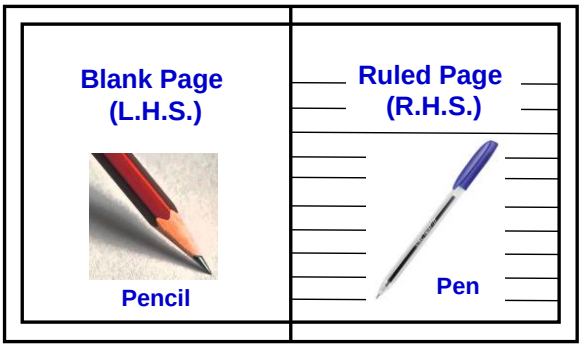


Fig. 1: Schematic representation of the pages in a conventional laboratory

1. On the **title** page, please write your **name, roll number, group code, course code, and the course name**.

2. The **index page** essentially serves as a **'table of contents'** and gives a very brief overview of the sequence of list of experiments that are performed on a particular date. ***The students are advised to fill up the index page promptly whenever they carry out an experiment***.

3. The student **MUST** fill up the **date, experiment number** and the **page number** on the top of the ruled page. A chronological, page-wise list of experimental write-up is being tabulated:

Blank Page (L.H.S.)	Ruled Page (R.H.S.)
Date:_____ (date on which the experiment is actually performed) **Experiment No.** _____ **Experiment:** (Name of the Experiment) **Apparatus:** **Chemicals required:** **Chemical reactions and /or Chemical structures** (Where applicable) **Indicator:** (Where applicable) **End point:** **(i.e., Change in colour at the end point)** **Observations:** (with proper units) **Calculations:** (Based upon the values obtained during experimentation/observation)**/Graph** **Result:** (with proper units; Report the result(s) as required in the aim of experiment)	**Experiment /Aim:** (Name of Experiment) **Theory:** **Chemical equations:** (where applicable) **Procedure:** **General Calculations:** **Result:** (with proper units) **Precautions:**

❖ Drawing a graph properly and interpreting results

As mentioned earlier, the student is required to perform a few **instrument-based experiments**. After the data is noted/ recorded, the students will be required to **plot the data-points** on a graph sheet using a pencil and **join the points** which will result in a particular **graphical pattern**. The graph, hence generated, will be consequently used to **interpret the results**.

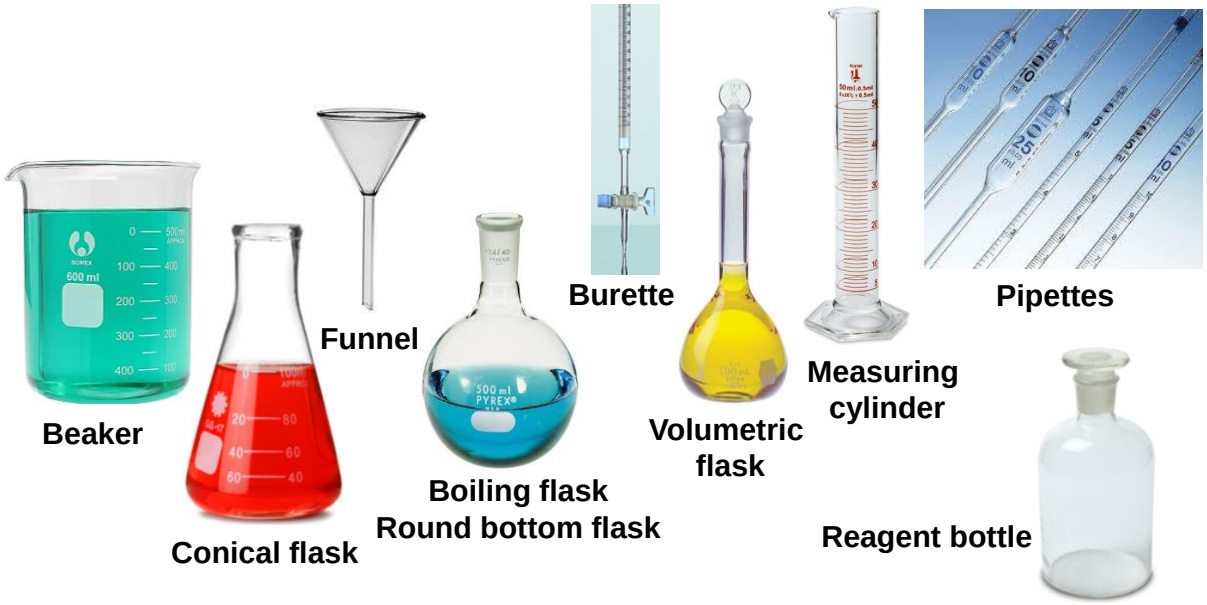
A few tips for the preparation of a good graph:

1. While labeling the axes (X, Y), please ensure that you have included the units of the variables properly, wherever it is applicable. A graph without any units is obscure and does not give an idea about the measureable quantities, volumes etc. that are required and used in an experiment.
2. Mark the XY-data-points on the graph.
3. Interpretation of an accurate and precise result from a graph is very important for an instrument-based experiment. However, while joining the data-points, please ensure from your instructor and/or teaching associate whether a ruler/scale is needed by you. Here are a few basic rules for joining the data-points:

- Certain graphical analysis requires drawing more than one slope and finding their intersection points.
- **REMEMBER**: When you join the data-points using a ruler/scale to draw a straight line or a slope, please **DO** ensure that the line/slope passes through a maximum number of data-points. It does not matter and it is absolutely **NOT** essential that all of the data-points have to fall on the straight line. It is **OKAY** if two/three data-points fall outside the line/slope. So, place your ruler in a few different ways to find out the best possible way of drawing a line/slope.
- A few graphs require joining the data-points by freehand drawing. Please **DO NOT** worry if one of the data-points does not fall onto the graph. It could be an experimental error/artefact which is caused involuntarily.

Commonly used Glassware in this Practical Course

Glassware are containers made up of glass and are commonly used in a chemistry laboratory because of the following reasons: Glass is (a) chemically-resistant (b) heat-resistant and (c) transparent. While carrying out the experiments, you will frequently use some glassware in the laboratory. It is always important and useful to know their proper names. Also, **please make sure that you wash/clean any glassware thoroughly before, and after each experiment.**



General precautions / important points to take care during experimentation

- Rinse the pipette (with the solution to be transferred to titration flask).
- Rinse the burette (with the solution to be taken/filled in the burette).
- Donot rinse the conical/titration flask.
- Upper meniscus to be read for coloured solutions.
- Lower meniscus to be read for colourless solutions.
- End point (signifies the change in colour of the solution e.g., from pink to colourless).

Chemical Structures of Commonly used Indicators

Indicators are defined as chemical sensors/detectors, required in extremely small quantities in a solution, which detect the changes in pH, redox potential, metal-ion complex formation, etc. Here, we shall discuss primarily two types of indicators that are going to be used in the practicals:

(1) pH-based indicators: These indicators are weak, conjugated organic acids that detect the changes in pH of a solution, especially after the completion of a titration. Since the indicator is a weak acid (HIn), an equilibrium will be established as this acid dissociates in an aqueous solution and the dissociation constant can be represented as shown in the schematic representation (Fig. 2). According to the Le Chatelier's principle, at lower pH (acidic condition),

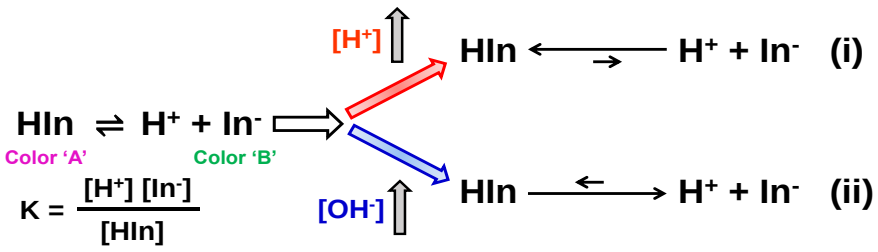
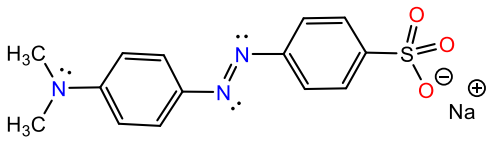
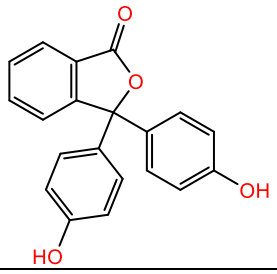


Fig. 2: Schematic representation of the effects of pH on a pH-based indicator. 'K' is the dissociation

the species 'HIn' will be predominant (eq. (i)) in the aqueous solution which can be detected by its color 'A' (Fig. 2). On the other hand, at higher pH (alkaline condition), the species 'In^-' will

be predominant (eq. (ii)), since the H^+ ions (released by HIn) will combine with OH^- to form water and hence, will get depleted progressively resulting in further enhancement in the dissociation (forward reaction). The predominance of In^- can be easily detected by its color 'B' (Fig. 2) in the aqueous solution. During an acid-base titration, a pH-based indicator is used that changes its color exactly at the end-point of the titration. The changes in color occur due to changes in the extent of conjugation upon protonation-deprotonation of one or more of the chemical moieties/substituents in HIn. However, this must be noted that there **DOES NOT** exist any universal pH indicator which works across the entire pH range.

Following is a list of a few pH-based indicators:

S. No.	Names	Chemical structure of pH indicator	pH range	Colour (pH) Acidic to Basic
1.	Methyl Orange		3.1 -4.4	Red to Yellow
2.	Phenolphthalein		8.2 - 10	Colourless to Pink

(2) Complexometric indicators: These indicators are weak, conjugated organic acids that detect binding of a metal-ion to a ligand leading to a metal-ligand complex formation in a solution. Typically, these indicators are functional at a given pH of the solution and they undergo a color change as the binding occurs. For example, Eriochrome Black-T (EBT) detects the complex formation between Ca^{2+}/Mg^{2+} and Ethylenediaminetetraacetic acid (EDTA) at pH 10 and its color changes from wine-red to blue. The utility and properties of EBT (in detail) is given in experiment no. 2 of this manual.

List of Experiments for B.E. (First year)

Session: 2018-19

1. To determine the amount of NaOH and Na_2CO_3 present in the same solution.
2. To find the temporary and permanent hardness of water sample by complexometric titration using standard EDTA solution.
3. To determine the copper content of a given sample solution of copper ore using 0.1 N sodium thiosulphate solution iodometrically.
4. To estimate the available chlorine in bleaching powder.
5. To determine the amount of Fe^{+2} and Fe^{+3} ions by permanganometry.
6. To find out the total alkalinity and sulphate content in a water sample.
7. To determine the strength of given sodium hydroxide solution by titration with standard hydrochloric acid conductometrically.
8. Determine pK_a value of acetic acid by pH-metric titration.
9. Spectrophotometric determination of Fe^{2+} with 1,10-phenanthroline.
10. To titrate potentiometrically FAS solution against potassium permanganate and to determine the standard electrode potential of Fe^{2+} / Fe^{3+} system.
11. To determine the total cation concentration in natural water.
12. Determination of cloud and pour point of given oil sample (Demonstration only).

EXPERIMENT NO. 1

EXPERIMENT: To determine the amount of NaOH and Na_2CO_3 present in the same solution.

APPARATUS: Pipette, burette, beakers, conical flask, funnel, burette stand and clamp.

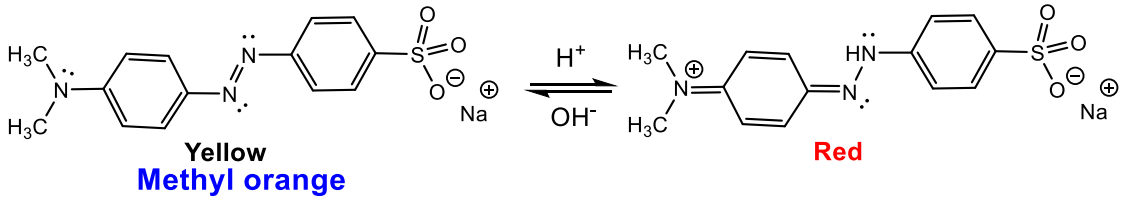
CHEMICALS: Sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), hydrochloric acid (HCl), methyl orange and phenolphthalein.

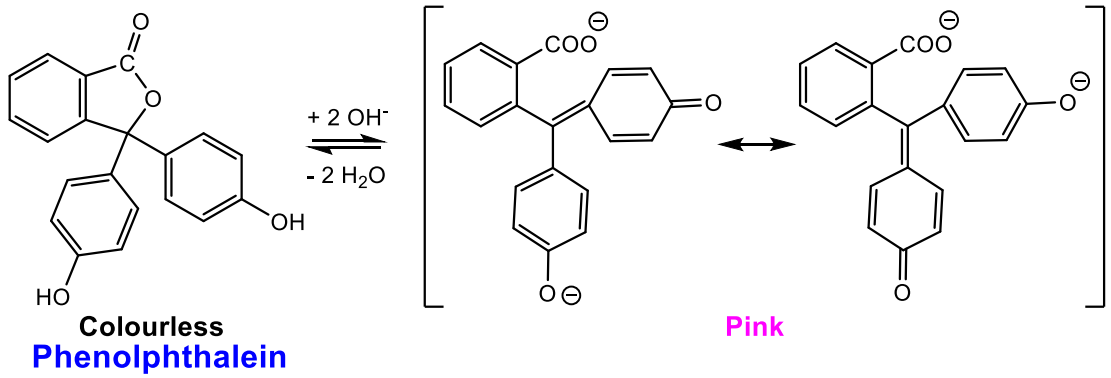
THEORY: When a mixture of NaOH and Na_2CO_3 is titrated against a standard HCl solution, colour of solution changes from yellow to pink (using methyl orange as an indicator) due to complete neutralization of both the alkalis at pH ≈ 4. However, when the mixture is titrated using phenolphthalein as an indicator, the colour of the solution changes from pink to colorless due to complete neutralization of NaOH and half neutralization of Na_2CO_3 (i.e., upto the conversion of Na_2CO_3 to $NaHCO_3$) at pH ≈ 8. The difference of two titre values gives the amount of HCl required for half neutralization of Na_2CO_3 while the difference of first titre value and twice the second titre value gives the amount of HCl required for NaOH neutralization.

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

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O$$





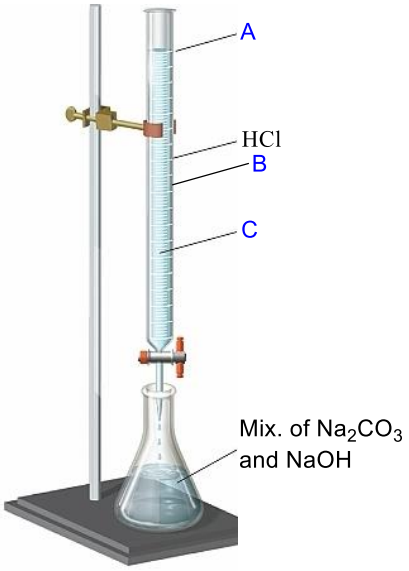
PROCEDURE

(i) Standardization of HCl

1. Transfer 10 mL of standard 0.1N Na_2CO_3 solution in a clean conical flask using a pipette.
2. Add 2 drops of methyl orange indicator. Titrate the solution against HCl from the burette.
3. The color of the solution changes from ***yellow to pink*** **(end point).**
4. Note the volume of the solution used and repeat the titration at least 4 times and take the mean of the closely related readings (V_o).

(ii) Determination of NaOH and Na_2CO_3 content

1. Transfer 10 mL of mixture of alkali solution into a conical flask.
2. Add 2-3 drops of phenolphthalein indicator. The solution ***becomes pink*** in color.
3. Note the initial reading of HCl from the burette (A). Titrate the solution with standard HCl while the solution becomes ***colorless*** (B).
4. Note the titre value and this is the phenolphthalein end point, **P**. **To the same solution,** add 2-3 drops of methyl orange indicator and continue the titration with HCl, until a sharp color change occurs from ***yellow to red*** at the end point (C).
5. This titre value i.e., the total volume of HCl run down from the beginning of the experiment to the methyl orange end point is noted and this is the methyl orange end point, **M**.



P = B - A
M = C - A

OBSERVATIONS

(i) Standardization of HCl solution

Volume of 0.1 N Na_2CO_3 solution taken for each titration = 10 mL

Sr. No.	Burette reading (mL)		Volume of HCl used (mL)
	Initial	Final	
1.			
2.			
3.			
4.			

Mean volume of HCl used **(V_o)** = _____ (mL)

(ii) Determination of NaOH and Na_2CO_3 in the mixture

Volume of mixture of NaOH and Na_2CO_3 solution taken for each titration = 10 mL

Sr. No.	Burette Reading (mL)			Volume of HCl used (mL)	
	Initial (A)	Colourless with Phenolphthalein (B)	Reddish colour with Methyl orange (C)	**P** = B – A	**M** = C – A
1.					
2.					
3.					
4.					

Mean volume of HCl used for **P** = _____ (mL)

Mean volume of HCl used for **M** = _____ (mL)

As P corresponds to ½ neutralization of Na_2CO_3 and complete neutralization of NaOH

∴ Half of Na_2CO_3 = **M** – **P** (cf. chemical equations)

So, volume of HCl required for neutralization of Na_2CO_3 = 2(**M** – **P**) = $\mathbf{V_1}$

Volume of HCl required for neutralization of NaOH = **M** – 2(**M** – **P**) = 2**P** – **M** = $\mathbf{V_2}$

GENERAL CALCULATIONS

Standadisation of HCl

Volume of alkali solution (Na_2CO_3) taken = 10 ml

Normality of Na_2CO_3 = N_2 ; Volume of HCl used = V_o

Using the normality equation

$N_1 \times V_o = N_2 \times 10$

$N_1 = N_2 \times (10/V_o)$

Determination of Na_2CO_3 and NaOH

(i) Determination of NaOH

Equivalent weight of NaOH = 40

Hence 1L of 1N HCl = 40g of NaOH

Normality of HCl used = N_1

V_2 ml of N_1 HCl = $40 \times (V_2/1000) \times N_1$ = y_1 gm of NaOH.

This is the amount of NaOH present in 10mL of the give alkali mixture solution.

Strength of NaOH = $y_1 \times 1000/10 = 100 \times y_1$ gm/L.

(ii) Determination of Na_2CO_3

Equivalent weight of Na_2CO_3 = 53

Hence 1L of 1N HCl = 53 gm of Na_2CO_3

Normality of HCl used = N_1

V_1 mL of N_1 HCl = $53 \times (V_1/1000) \times N_1$ = y_2 gm of Na_2CO_3.

This is the amount of Na_2CO_3 present in 10mL of the given alkali mixture solution.

Strength of $Na_2CO_3 = y_2 \times (1000/10) = 100 \times y_2$ gm/L.

RESULTS: The given alkali mixture contains NaOH = $100 \times y_1$ gm/L

The given alkali mixture contains $Na_2CO_3 = 100 \times y_2$ gm/L.

Expected CLOs/Daily life application: The total basic content of an antacid tablet can be determined in a similar manner.

EXPERIMENT NO. 2

EXPERIMENT: To find the temporary and permanent hardness of water sample by complexometric titration using standard EDTA solution.

APPARATUS: Pipette, burette, beakers, conical flask, funnel, burette stand and clamp.

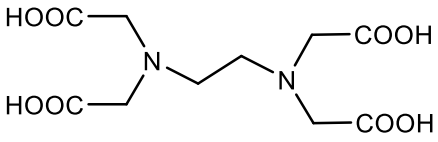
CHEMICALS: Water samples, ethylenediaminetetraacetic acid (EDTA), Eriochrome Black-T (EBT) indicator, ammonium hydroxide-ammonium chloride buffer of pH 10

THEORY: Hardness of water is due to the presence of soluble salts of Ca and Mg. It is an important parameter to judge the quality of water. Determination of hardness of water by EDTA titration is a very accurate method based on the fact that when Eriochrome black-T (EBT; blue dye) is added to the hard water (at about pH 10), it gives a wine red colored unstable complex with Ca^{2+}/Mg^{2+} ions.

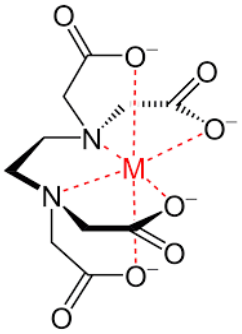
$$\underset{}{Ca^{2+}/Mg^{2+}} + \underset{\text{Blue dye}}{\text{EBT}} \xrightarrow{\text{pH 10}} \underset{\text{Wine red (Unstable complex)}}{Ca^{2+}/Mg^{2+}\ \text{EBT complex}}$$

Temporary hardnesss in a water sample is caused by bicarbonates of hardness producing ions (Ca^{2+} and Mg^{2+}). This can be removed by prolonged boiling due to decomposition of bicarbonates with the evaluation of CO_2 and simultaneous precipitation of the respective carbonates. When EDTA (ethylene diammine tetraacetic acid) solution is added to the hard water (with permanent or temporary hardness), the unstable wine red complex of Ca^{2+}/Mg^{2+}-Eriochrome black-T breaks and a stable complex of Ca^{2+}/Mg^{2+} with EDTA is formed resulting in change of color of the solution from wine red to blue at the end point.

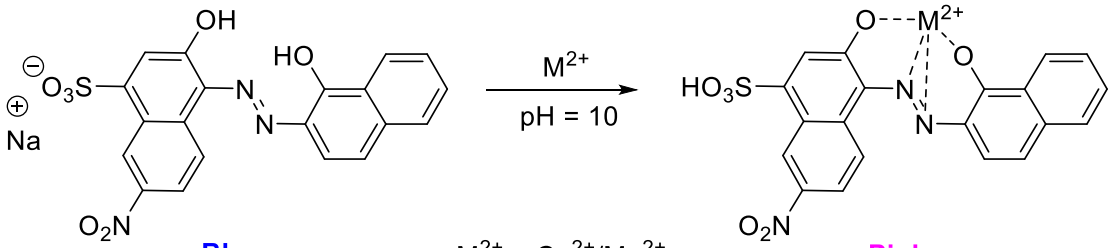
$$\underset{\text{Wine red (Unstable complex)}}{Ca^{2+}/Mg^{2+}\ \text{EBT complex}} + \text{EDTA} \xrightarrow{\text{pH 10}} \underset{\text{Colourless}}{Ca^{2+}/Mg^{2+}\ \text{EDTA complex}} + \underset{\text{Blue dye}}{\text{EBT}}$$



EDTA



Metal-EDTA complex



Blue

Erichrome Black T

$M^{2+} = Ca^{2+}/Mg^{2+}$

Pink

PROCEDURE

Preparation of standard hard water: Dissolve 1 gm of pure dry $CaCO_3$ in minimum quantity of dilute HCl. Evaporate the solution to dryness on a water bath to remove excess of acid. Dilute the contents with distilled water to make 1L. Each mL of this solution contains 1 mg of $CaCO_3$, i.e., hardness of this solution is 1000 ppm (0.01 M). This solution is used to standardize the EDTA solution.

Standardization of EDTA

1. Rinse the titration flask with distilled water and transfer 10mL of the standard hard water sample (0.01 M) into it using a pipette.
2. Add about 2-3mL of ammonia/ammonium chloride buffer solution and 2-3 drops of the EBT indicator. The color of solution becomes wine red.
3. Titrate the hard water against the EDTA solution, till the wine ***red color changes to blue.*** Note the burette reading (V_0 mL).
4. Repeat the procedure until three concordant readings are obtained.

Determination of total hardness of water sample

Rinse the titration flask with distilled water and transfer 10mL of the given water sample into it using a pipette. Follow the steps 2 – 4 given above (for the standardization of EDTA). Let the titre value corresponding to total hardness of water sample be V_1.

Determination of permanent hardness

Measure 100 mL of hard water sample into 500 mL beaker, boil gently for 30-35 minutes. Filter the solution into a 100 mL measuring flask. Make up the solution up to the mark with de-ionized water and mix thoroughly.

Rinse the titration flask with distilled water and transfer 10mL of this (boiled-water) sample into it using a pipette. Follow the steps 2 – 4 as above (for the standardization of EDTA). Let the titre value corresponding to total hardness of water sample be V_2.

Determination of temporary hardness

Difference between the two values ($V_1 – V_2$) corresponds to temporary hardness.

OBSERVATIONS

(i) Standardization of EDTA solution

Volume of 0.01 M standard hard water solution taken for each titration = 10 mL

Sr. No.	Burette reading (mL)		Volume of EDTA used (mL)
	Initial	Final	
1.			
2.			
3.			
4.			

Mean volume of EDTA used (V_0) = _____ (mL)

(ii) Determination of total hardness

Volume of hard water sample (unknown) taken for each titration = 10 mL

Sr. No.	Burette reading (mL)		Volume of EDTA used (mL)
	Initial	Final	
1.			
2.			
3.			
4.			

Mean volume of EDTA used (V_1) = _____ (mL)

(iii) Determination of permanent hardness

Volume of boiled hard water sample taken for each titration = 10 mL

Sr. No.	Burette reading (mL)		Volume of EDTA used (mL)
	Initial	Final	
1.			
2.			
3.			
4.			

Mean volume of EDTA used (V_2)= _____ (mL)

GENERAL CALCULATIONS

(i) Determining the molarity of EDTA solution

Applying the molarity equation

(Standard Hard water) (EDTA)

$0.01 \times 10 = M_1 \times V_0$

Molarity of the EDTA, $M_1 = (0.01 \times 10)/V_0$

(ii) Determination of total hardness

Molarity of EDTA = M_1

Applying the molarity equation

(Hard water) (EDTA)

$M_2 \times 10 = M_1 \times V_1$

Molarity of the hard water, $M_2 = (M_1V_1)/10$

Hardness of water sample, Y = Molarity × Molecular weight of $CaCO_3$

Hardness of water sample, Y = $(M_1V_1)/10 \times 100$ (Molecular weight of $CaCO_3$) gm/L

= $(M_1V_1)/10 \times 100$ (Molecular weight of $CaCO_3$) × 1000 mg/L

Total Hardness = Y ppm (mg/L)

(iii) <u>Determination of permanent hardness</u>

Again apply the molarity equation

(Boiled Hard water) (EDTA)

$M_3 \times V_1 = M_1 \times V_2$

M_3 = (Molarity of hard water due to permanent hardness)

Molarity of the hard water, $M_3 = (M_1V_2)/10$

Permanent hardness of water sample, Z = Molarity × Mol. wt. of $CaCO_3$

Permanent hardness of water sample, $Z = (M_1V_2)/10 \times 100$ (Mol. wt of $CaCO_3$) gm/L

$= (M_1V_2)/10 \times 100$ (Mol. wt of $CaCO_3$) × 1000 mg/L

Permanent hardness = Z ppm (mg/L)

(iii) <u>Temporary hardness</u>: Total hardness – Permanent hardness = (Y − Z) ppm

<u>RESULTS</u>: Total hardness = Y ppm

Permanent hardness = Z ppm

Temporary hardness = (Y − Z) ppm

<u>PRECATIONS</u>

(1) Wash the titration flask with distilled water each time, before transferring hard/ sample water solution.

(2) Continue the titration till the complete removal of wine-red tinge in the solution.

<u>Expected CLOs/Daily life application</u>: Determination of hardness of water can help in industrial settings, where water hardness is monitored to avoid costly breakdowns in boilers, cooling towers, and other equipment. High calcium levels also cause irritation in eyes. Hence, quantification of ions in potable water is necessary.

EXPERIMENT NO. 3

EXPERIMENT: To determine the copper content of a given sample of copper ore solution using 0.1 N sodium thiosulphate iodometrically.

APPARATUS: Pipette, burette, beakers, conical flask, funnel, burette stand and clamp.

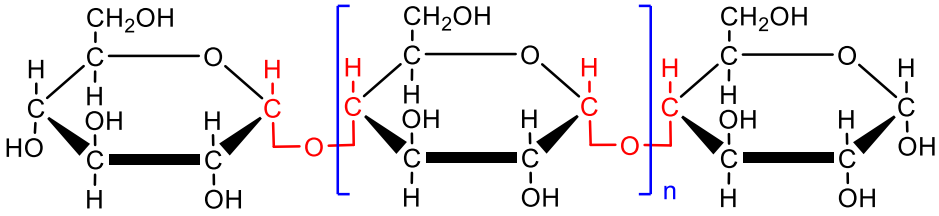
CHEMICALS: Copper sulfate ($CuSO_4$), solid sodium bicarbonate ($NaHCO_3$), acetic acid (CH_3COOH), potassium iodide (KI), starch solution and sodium thiosulfate ($Na_2S_2O_3$).

THEORY: Estimation of copper in the copper ore is based on the fact that copper can quantitatively liberate iodine from potassium iodide solution in an acidic medium. The liberated iodine can be titrated against a given standard sodium thiosulphate solution using starch as an indicator.

$$2\ CuSO_4 + 4KI \xrightarrow{H^+} 2\ CuI_2 + 2\ K_2SO_4$$

$$2CuI_2 \longrightarrow Cu_2I_2\downarrow + I_2$$

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



Starch

End point is the appearance of white color due to precipitates of Cu_2I_2. As Cu_2I_2 is soluble in mineral acids but insoluble in weak organic acids (acetic acid), the strongly acidic medium is neutralized with $NaHCO_3$ till a faint permanent precipitates of basic copper carbonate are formed which are dissolved with a few drops of acetic acid.

PROCEDURE

1. Pipette out 10 ml of the copper ore solution into a titration flask.

2. Add small amount of some solid $NaHCO_3$ to the ore solution in small doses till there is no effervescence. The solution turns milky at this stage.

3. Add dilute acetic acid dropwise, just sufficient to remove the milkiness. To the clear blue solution, add 5 ml of 10 % KI solution. Color of the solution changes to ***dark brown***, due to the formation of KI_3.

4. Add about 35 ml of distilled water to dilute the contents of the flask. Wait for atleast 3 minutes. Titrate the solution against standard sodium thiosulphate solution till the ***color turns to pale/ light yellow.***

5. Add about 2 ml of 1% freshly prepared starch solution. Color of the solution turns to ***deep blue.***

6. Continue the titration (**same conical flask**) with more sodium thiosulphate solution till the ***color changes from blue to permanent white***.

7. Keep the contents of the flask for some time on the table-shelf. It should not turn blue again. If this happens, add a few more drops of $Na_2S_2O_3$ solution to get permanent white color again.

8. Repeat the experiment to get atleast five correct readings till atleast two concordant readings are obtained.

OBSERVATIONS

Volume of copper ore solution taken for each titration = 10 ml

Sr. No.	Burette Reading (mL)		Volume of 0.1 N $Na_2S_2O_3$ soln. added (mL)
	Initial	Final	
1.			
2.			
3.			
4.			

Mean volume of $Na_2S_2O_3$ used = (V_2) _____ mL

GENERAL CALCULATIONS

Volume of copper ore solution used for each titration (V_1) = 10ml

Normality of sodium thiosulphate solution = 0.1 N

Let volume of $Na_2S_2O_3$ used = V_2 ml

Applying the normality equation

Copper ore $Na_2S_2O_3$

$N_1V_1 = N_2V_2$

10 ml of N_1 copper ore solution = V_2 ml of 0.1 N $Na_2S_2O_3$ solution

N_1 [Normality of copper solution] = $(0.1 \times V_2)/10 = V_2$

Eq. wt. of copper = 63.50

Amount of copper in the given ore = $N_1 \times 63.5$ gm/L

RESULT: The amount of the copper present in copper ore solution is ____ gm/L.

PRECATIONS

1. The white color at the end point should be permanent.
2. The copper ore solution should be neutralized before titration.
3. The contents of the titration flask should be diluted to observe better change of color at the end point.
4. After mixing the initial solutions, wait for atleast 3 minutes before starting the titration.
5. General precautions of volumetric titrations should be followed.

Expected CLOs/Daily life application: As both excess and low levels of copper can have adverse effect, e.g., excess of copper in body can cause “Wilson Disease”. Hence copper levels should be checked regularly.

EXPERIMENT NO. 4

EXPERIMENT: To estimate available chlorine in the bleaching powder.

APPARATUS: Pipette, burette, beakers, conical flask, funnel, burette stand and clamp, volumetric flask.

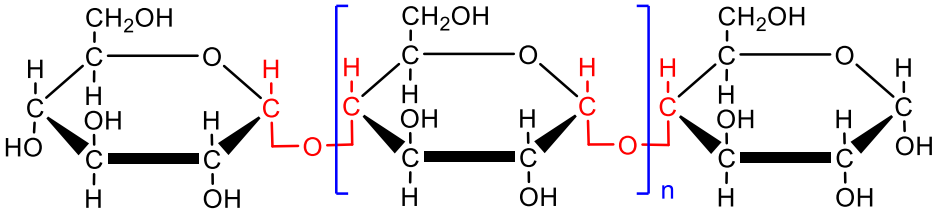
CHEMICALS: Bleaching powder, Glacial Acetic acid, 0.1N Sodium thiosulphate, Potassium Iodide, starch.

THEORY: Bleaching powder is frequently utilized as a decontaminator. But upon standing it gets decomposed and its total chlorine content gets reduced. So, it's very important to find out exact chlorine content in order to know the exact amount of bleaching powder required for practical purposes.

$$Ca(OCl)Cl + CH_3COOH \longrightarrow (CH_3COO)_2Ca + Cl_2 + H_2O$$

$$Cl_2 + 2\,KI \longrightarrow 2KCl + I_2$$

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



Starch

Bleaching powder liberates chlorine under weakly acidic condition. The liberated chlorine can be treated with excess KI to release equivalent amount of iodine that can be estimated by titrating against standard sodium thiosulphate solution using starch as indicator.

PROCEDURE

1. Dissolve accurately about 0.4 g of bleaching powder in water to obtain a milky white solution in a 250 ml volumetric flask.

2. Pipette out 25 ml of the above solution and add 5ml of glacial acetic acid and 5 ml of 10 % KI solution. Color of the solution changes to ***dark brown***, due to the formation of KI_3.

4. Add about 100 ml of distilled water to dilute the contents of the flask. Wait for at least 3 minutes. Titrate the solution against standard sodium thiosulphate solution till the ***color turns to***

pale/ light yellow.

5. Add about 2 ml of 1% freshly prepared starch solution. Color of the solution turns to ***deep blue.***

6. Continue the titration (**same conical flask**) with more sodium thiosulphate solution till the ***color changes from blue to permanent white***.

7. Keep the contents of the flask for some time on the table-shelf. It should not turn blue again. If this happens, add a few more drops of $Na_2S_2O_3$ solution to get permanent white color again.

8. Repeat the experiment to get at least five correct readings till at least two concordant readings are obtained.

OBSERVATIONS

Volume of bleaching powder solution taken for titration = 25 mL

Sr No	Burette Reading (mL)		Volume of Sodium thiosulphate used (mL)
	Initial	Final	
1.			
2.			

Mean volume of Sodium thiosulphate used = V _____ (mL)

GENERAL CALCULATIONS

Determination Chlorine content

Amount of Bleaching powder taken (in gram) = A

25 ml of bleaching powder solution = V ml of 0.1N sodium thiosulphate solution

Strength of bleaching powder solution = = (0.1 x V)/25 = S(N)

Equivalent weight of chlorine = 35.46

1000 ml S(N) bleaching powder contains 35.46 x S g of available chlorine

Then,

250 ml S(N) bleaching powder contains (35.46 x S x 250)/1000 g of available chlorine = G g of available chlorine

% of Available Chlorine = (Gx100)/A

RESULT: The amount available chorine in bleaching powder solution is found to be ….%

EXPERIMENT NO. 5

EXPERIMENT: To determine the amount of Fe^{+2} and Fe^{+3} ions by permanganometry.

APPARATUS: Pipette, burette, beakers, conical flask, funnel, burette stand and clamp.

CHEMICALS: Mohr's salt solution (Ferrous ammonium sulfate; $FeSO_4(NH_4)_2SO_4.6H_2O$)), permanganate ($KMnO_4$) and sulphuric acid (H_2SO_4).

THEORY: Mn^{7+} oxidises Fe^{+2} in acidic medium to Fe^{3+} and itself gets reduced to divalent chromium (Mn^{2+})

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

$KMnO_4$ acts as a self-indicator. If Fe^{3+} is present in the original solution, it can be reduced by boiling the solution with zinc pieces in acidic medium and can be titrated with standard $KMnO_4$. The end point in this case corresponds to presence of both Fe^{+2} and Fe^{+3} ions in the solution.

PROCEDURE

(i) Standardization of $KMnO_4$

1. Transfer 10 mL of the standard 0.1 N ferrous ammonium sulfate (FAS) solution to a clean conical flask using a pipette.
2. Add 5 mL of 4 N sulphuric acid.
3. Titrate the solution against $KMnO_4$ solution taken in a burette. The color of the solution changes from ***colorless to pink***.
4. Note the volume of the solution used and repeat the titration at least 5 times and take the mean of the closely related readings (V_1).

(ii) Determination of Fe^{+2}

1. Pipette out 10 ml of the given solution in the titration/ conical flask.
2. Add 5 mL of 4 N sulphuric acid.
3. Titrate the solution against $KMnO_4$ solution taken in a burette. The color of the solution changes from ***colorless to pink***.

4. Note the volume of the solution used and repeat the titration at least 5 times and take the mean of the closely related readings (V_2).

(iii) Determination of Fe^{+2} and Fe^{+3} (Total iron content)

1. Pipette out 10 ml of aqueous solution into the conical flask. [The given solution has already been boiled with 2-3 grams of zinc pieces and 5 mL of dilute H_2SO_4 to reduce the Fe^{3+} to Fe^{2+}].
2. Add 5 ml of 4N H_2SO_4.
3. Titrate it with standard $KMnO_4$ solution till the solution turns from ***colorless to pink***.
4. Note the volume of the solution used and repeat the titration at least 5 times and take the mean of the closely related readings (V_3).

GENERAL CALCULATIONS

GENERAL CALCULATIONS

(i) Normality of $KMnO_4$ solution

Apply the Normality equation

($KMnO_4$) (FAS)

$N_1V_1 = N_2V = 0.1\ N \times 10\ mL$

Normality of the $KMnO_4$ $N_1 = (0.1 \times 10)/V_1 = S\ (N)$

(i) Determination of Fe^{+2}

Vol. of solution taken = 10 mL

Vol. of $KMnO_4$ solution used = V_2 mL

Normality of $KMnO_4$ = S N

Normality of Fe^{2+}

$$N_1 = \frac{V_2 \times S}{10}$$

Strength of Fe^{2+} = N_1 x Eq. wt.

= N_1 x 56 gm/L

(ii) Determination Fe^{+3} in a mixture of Fe^{+2} and Fe^{+3}

Vol. of solution taken = 10 mL

Vol. of $KMnO_4$ solution used = V_3 mL

Normality of $KMnO_4$ = S N

Normality of total Fe

$$N_1 = \frac{V_3 \times S}{10}$$

Strength of total Fe = N_1 x Eq. wt.

= N_1 x 56 gm/L

Strength of Fe^{+3} ions = Normality × Eq. wt.

$$= \frac{(V_3 - V_2) \times S \times 56}{10}$$

RESULTS: The amount of Fe^{+2} = _____ gm/L ; and the amount of Fe^{+3} = _____ gm/L.

Expected CLOs/Daily life application: In qualitative and quantitative determination of Fe^{2+} and/or Fe^{3+} present in an ore or compound, water sample etc.

EXPERIMENT NO. 6

EXPERIMENT: To find out the total alkalinity and sulphate content in a water sample.

APPARATUS: Pipette, burette, beakers, conical flask, funnel, burette stand and clamp.

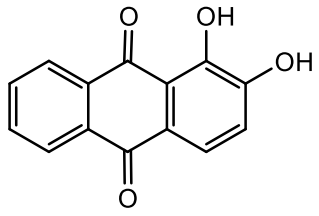
CHEMICALS: Water samples, Alizarin Red Indicator, Barium Chloride ($BaCl_2$), methyl orange and sulphuric acid (H_2SO_4).

THEORY: Alkalinity of water is due to the presence of hydroxides, carbonates and bicarbonates of the salts of calcium, magnesium, sodium and potassium. Similarly, the chloride content of water is due to the presence of chloride ions of these cations. Total alkalinity is estimated by titrating a known volume of water against a standard acid (N/20 H_2SO_4) using methyl orange as indicator in the neutral medium.

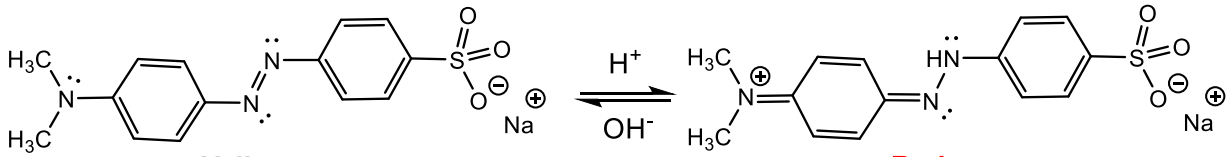
$$CO_3^{2-} + 2H^+ \longrightarrow CO_2 + H_2O$$

$$HCO_3^- + H^+ \longrightarrow CO_2 + H_2O$$

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



Alizarin



Yellow

Methyl orange

Red

Sulphate content is estimated by titrating a known volume against a standard barium chloride solution (N/100) using alizarine red as indicator.

PROCEDURE

(i) Determination of total alkalinity of tap water

1. Wash, rinse and fill the burette with N/20 H_2SO_4.

2. Transfer 100 ml of tap water in the titration flask. Add 2-3 drops of methyl orange and titrate it against N/20 H_2SO_4 till the colour changes from ***yellow*** to ***light pink***, as an end point.

3. Note the volume of the solution used and repeat the titration at least 5 times and take the mean of the closely related readings (x ml).

(ii) Determination of sulphate contents of water sample

1. Take 10 ml of water sample in a titration flask.
2. Add 3-4 drops of alizarine red and titrate against N/100 $BaCl_2$ from the burette till the color changes from **yellow to pink**.
3. Note the volume of the solution used and repeat the titration at least 5 times and take the mean of the closely related readings (y ml).

OBSERVATIONS

Let the volume of N/20 H_2SO_4 used = x ml

Let the volume of N/100 $BaCl_2$ used = y ml

GENERAL CALCULATIONS

(i) Alkalinity

Applying the normality equation

(Tap water) (H_2SO_4)

$N_1V_1 = N_2V_2$

100 ml of tap water (of normality N_1) = x ml of N/20 H_2SO_4

$$N_1 = \frac{N_2V_2}{V_1} = \frac{0.05\,x}{100} = \frac{x}{2000}$$

Eq. wt. of $CaCO_3$ = 50 ; Amount of $CaCO_3$ (gm/L) = Normality × Eq. wt.

$$= \frac{x}{2000} \text{x } 50 = \frac{x}{40}$$

Amount of $CaCO_3$ (mg/1000 mL)

$$= \frac{x}{40} \text{x } 1000\ ppm$$

(ii) Sulphate Content

Applying the normality equation,

(Tap water) ($BaCl_2$)

$N_1V_1 = N_2V_2$

10 ml of tap water (of normality N_1) = y ml of N/100 $BaCl_2$ solution

$$N_1 = \frac{N_2V_2}{V_1} = \frac{y}{1000}$$

Eq. wt. of SO_4^{2-} = 48.03

Sulphate Content (gm/L) = Normality × Eq. wt.

$$= \frac{y}{1000} \text{ x } 48.03$$

Chloride Content (mg/1000 mL) = $y \times 48.03$ *ppm*

RESULTS

Amount of total alkalinity in water sample _____ ppm of $CaCO_3$

Amount of sulphate content in water sample _____ ppm

Expected CLOs/Daily life application: Alkalinity and chloride ion is important for aquatic life as it helps in maintaining pH. However, highly alkaline water can corrode the pipelines. Alkaline water is helpful in recovering petroleum too. Also, to maintain quality of potable water, quantification of both alkalinity and chloride ions is crucial.

EXPERIMENT NO. 7

EXPERIMENT: Determine the strength of sodium hydroxide solution by titration with standard hydrochloric acid (0.1 N) conductometrically.

APPARATUS: Pipette, burette, beakers, funnel, burette stand, clamp, conductometer and conductivity cell.

CHEMICALS: Standard hydrochloric acid (HCl) and sodium hydroxide (NaOH).

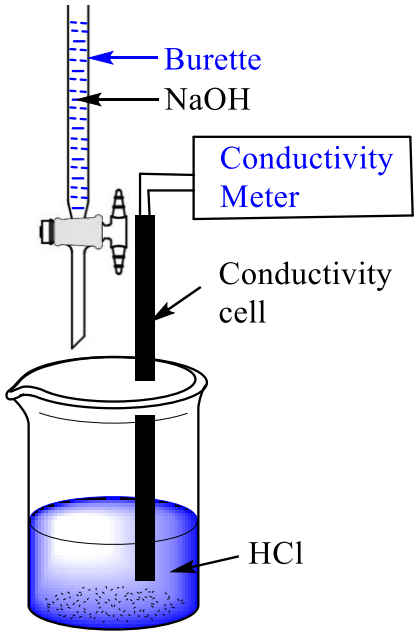
THEORY: There is a decrease in H^+ ion concentration upon addition of NaOH solution to the HCl solution, resulting in decrease in conductivity of the solution.

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

During titration, conductivity of solution first decreases upto equivalence point, then increases due to increase in hydroxyl ion concentration. Initally, with the addition of the alkali to the acid there will be a decrease in conductance. After the neutralization is complete, further addition of alkali would result in increase of conductance, since the additional OH^- ions from NaOH are no longer used up in the chemical reaction. So, if we plot conductivity versus volume of titrant/ NaOH, we get V shaped curve. From the titration curve an equivalence point can be obtained.

PROCEDURE

1. Take 50 ml of HCl solution in a clean beaker and immerse/dip the conductivity cell in it. Make sure that the two platinum electrodes of the cell are completely dipped in the solution.
2. Connect the cell to the bridge. Note down the conductivity.
3. Add NaOH from the burette at an interval of 0.5 ml each time, stir the contents and note down the conductivity every time. The conductivity will first decrease and then increase.
4. Plot the conductance against the volume of NaOH added. The equivalence point can be determined from the inter-section of two lines on the graph and hence the strength of NaOH solution can be calculated. This procedure can also be applied to find the strength of mixtures of two acids or bases and also in the precipitation titration.

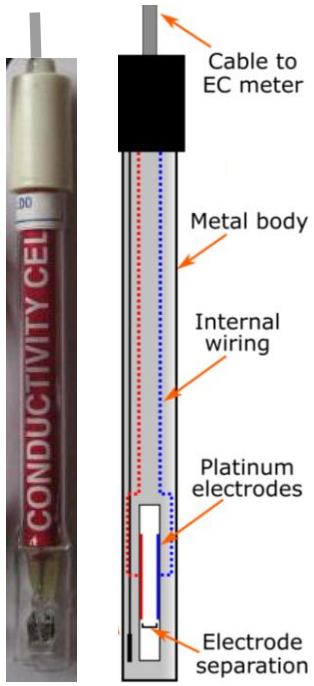


OBSERVATIONS

Volume of 0.1 N HCl taken in the beaker = 50 ml

Vol. of NaOH added from the Burette (mL)	Conductivity (millimho)

Draw a graph Conductance vs. Volume of NaOH (sample graph is as shown) and find out volume of NaOH required (i.e., point **A**) for the complete neutralization of 50 mL of HCl.

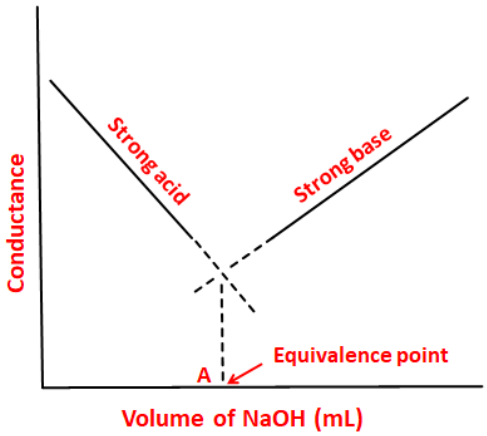


Conductivity Cell

Applying Normality Equation:

$$N_{NaOH} = N_{HCl} \times (50/ \mathbf{A})$$

Strength of NaOH (gm/L) = Normality × Eq. wt.



RESULT: The strength of sodium hydroxide present in the given sample is _____ gm/L

Expected CLOs/Daily life application:

- It can be used to check water pollution in lakes as well as rivers.
- It is also used to check the alkalinity of the fresh water.
- Salinity of the sea water can also be checked by this method.
- Used for tracing microorganism in food microbiology.
- To check the solubility of sparingly soluble salts.

EXPERIMENT NO. 8

EXPERIMENT: Determine pKa value of acetic acid by pH metric titration

APPARATUS: Pipette, burette, beakers, funnel, burette stand, clamp, pH meter and glass electrode.

CHEMICALS: Sodium hydroxide (NaOH) and acetic acid (CH_3COOH).

THEORY: A pH meter will be used to follow the titration of an unknown weak acid, HA (aq) with sodium hydroxide. NaOH (aq).

$$HA\ (aq) + NaOH\ (aq) \longrightarrow NaA\ (aq) + H_2O$$

The weak acid has a concentration around 0.1M. The result of the pH versus volume of NaOH plot is "S" shaped curve which is not as steep as the one arising from the titration of a strong acid. The equivalence point (this time) will be at alkaline pH (not 7 as in strong acid vs strong base). From the equivalence point, the concentration of an unknown acid HA is found. In addition, the acid constant K_a can be determined.

$$HA + H_2O \longrightarrow H_3O + A^-$$

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

$$pH = pKa + \log \frac{[\text{salt form}]}{[\text{acid form}]}$$

Henderson–Hasselbalch equation

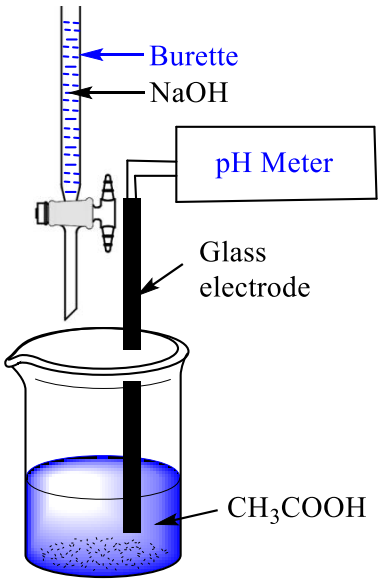
PROCEDURE

Titration of unknown HA with standard NaOH

1. Calibrate the pH meter with the standard buffer solution of pH = 4 or 9, then rinse the glass electrode and immerse it in the beaker. Position the burette so that the titrant can be easily added.

2. Pipette out 50 ml of acetic acid into a clean beaker, dip the glass electrode. Record the pH.

3. Initially, add 0.5 ml of 0.1 N NaOH solution at a time, record the pH (after each addition), until the pH change is more than 0.2–0.3 units, then start adding 0.2 ml of NaOH each time (i.e., near to the equivalence point, decrease the volume of NaOH added) so that the

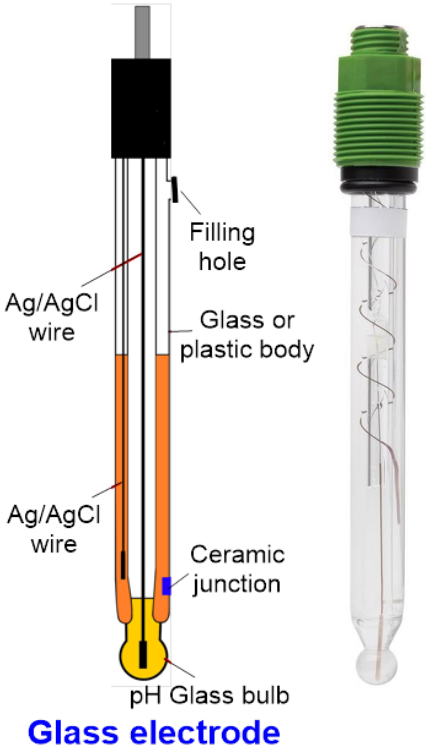


change in pH is small enough to yield a good shape of plot.

4. After the rapid change in pH (after the equivalent point), the volume of NaOH may again be increased to 0.5 ml per addition. Make at least 10 more additions after the equivalence point so that the region with the plateau can be plotted.

5. pK_a is determined by examining the titration curve. The negative log of K_a is pKa and is same ***as the pH at half the volume of equivalence point.***

(pH = pKa when logarithm term is zero which in turn is zero once [salt] = [acid]. This is true at half equivalence point) cf. Henderson–Hasselbalch equation.



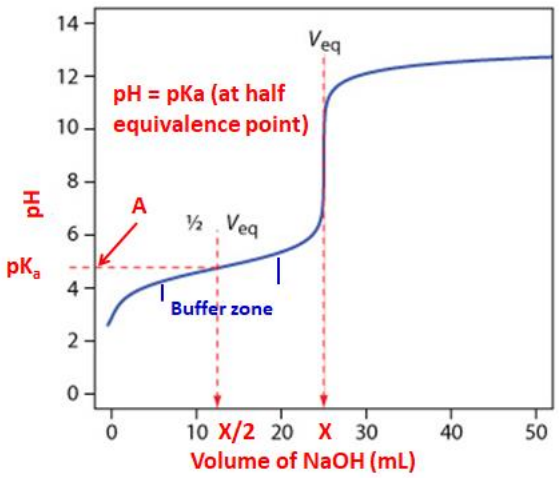
OBSERVATIONS

Normality of standard NaOH = 0.1 N

Vol. of NaOH added from the Burette (mL)	pH

Draw a graph pH vs. volumes of NaOH (sample graph is as shown). Find out pKa value of CH_3COOH from the graph as under:

NaOH (mL) at equivalence point	**NaOH (mL) at half equivalence point**	**pH (at half equivalence point) = pKa**
X (along x-axis)	$\frac{X}{2}$ (along x-axis)	pH at $\frac{X}{2}$ = **A** (along y-axis)



RESULT: The pKa of acetic acid is _____.

Expected CLOs/Daily life application: Knowledge of pK_a values is important for the quantitative treatment of systems involving acid–base equilibria in solution. Design of buffers (that resist any change in pH), drug development are couple of applications that require knowledge of pK_a.

EXPERIMENT NO. 9

EXPERIMENT: Spectrophotometric determination of iron(II) with 1,10-phenanthroline.

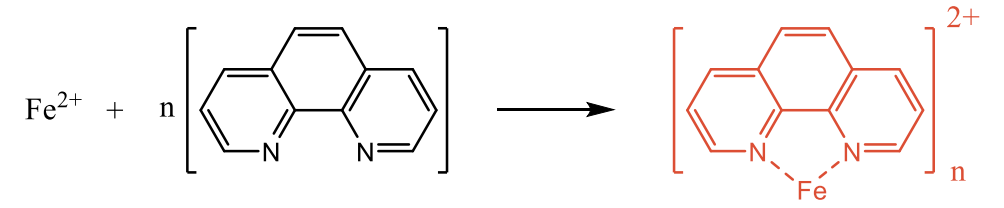
APPARATUS: Burette, volumetric flasks (50 mL), cuvettes, funnel, burette stand, clamp and colorimeter

CHEMICALS: Mohr's salt solution (Ferrous ammonium sulfate; $FeSO_4(NH_4)_2SO_4.6H_2O$), 1,10-phenanthroline, hydroxylamine hydrochloride, acetic acid-sodium acetate buffer of pH 4.5 and sulphuric acid (H_2SO_4).

THEORY: Iron(II) reacts with 1,10-phenanthroline to form an ***orange red*** complex $[(C_{12}H_8N_2)_3Fe]^{+2}$. The color intensity is independent of the acidity in pH range 2-9. If iron (III) is present it can be reduced with hydroxylamine hydrochloride. The absorbance is mentioned at a wavelength of 515 nm. The variation in the concentration of a given colored solution, changes the intensity of the transmitted light. The change in light intensity is measured by the instrument called photocolourimeter/ colourimeter. When monochromatic light falls on a solution sample, some light is absorbed and the intensity of the transmitted light is decreased. The decrease in intensity of light is proportional to the thickness of the absorbing medium and the concentration of solution. This may be expressed by Lambert-Beer law:

$$A = \log(1/T) = \log(I_o/I) = \varepsilon.b.c$$

Where c is the concentration of the solution expressed in mol/L and 'ε' is a constant characteristic of the solute and the wavelength of light, ε is called the molar extinction coefficient. 'A' is absorbance or optical density (D) of solution; *b* is path length and is related to the transmittance ($T = I/I_o$).



Colourless — Phenanthroline (Colourless) — Iron-phenanthroline complex (Reddish-orange colour)

n = number of phenanthroline molecules reacting with Fe^{2+}

PROCEDURE

A. Preparation of Samples

1. Take six 50 mL volumetric flasks and add 0, 1, 2, 3, 4, 5 ml of FAS solution in each flask. Let's name these volumetric flasks as **K, L, M, N, O and P.**
2. Then add 2 ml of 1,10-phenanthroline solution to each of these volumetric flasks.
3. Now dilute each volumetric flask with deionised water to afford a total volume of 50 mL (by filling the these flasks upto the mark). Stopper the flasks and mix the contents well by shaking vigorously for few minutes. Allow the solution to stand for 10 minutes.
4. The first volumetric flask to which 0 ml of FAS is added (i.e., no Fe^{2+} ions), will serve as a blank. (**Solution K**).

The Fe concentration in these flasks will be:

K	0.0 N
L	2.0×10^{-5} N
M	4.0×10^{-5} N

N	6.0×10^{-5} N
O	8.0×10^{-5} N
P	10.0×10^{-5} N

B. To determine the λ_{max}

1. Get the two cuvettes issued from the laboratory staff.
2. Fill one of them with the blank solution (**K**) and another one with the one of the samples containing Fe. Let's say **solution P.**
3. Light of single wavelength can be produced by selecting the filter on the photocolorimeter. Usually, the range goes from 410 nm–700 nm.
4. Set the filter to 410 nm. Place the cuvette filled with blank solution, **K**, in the sample holder.
5. Set the absorbance to 0%.
6. Now place the second cuvette, with solution **P**, in the sample holder. Measure the absorbance of the solution. Now you have the absorbance at 410 nm for solution **P**.
7. **By changing the filter to next wavelength each time, repeat steps 4–6. You need to set the absorbance to zero with blank (K) every time you change the wavelength with filter.**
8. Now, you have absorbance of solution P, over a range of wavelength from 410 nm-700 nm. You will notice that graph between the Absorbance and wavelength takes an ***inverse parabola shape***, with a maximum absorbance around 500 nm or 480 nm. This is your λ_{max}**.**

C. Measurement of Absorbance for Solutions L to P at λ_{max}

1. Set the filter to λ_{max} obtained in part B (step 8).
2. Set the absorbance to 0 using your blank sample (**K**).
3. Measure the absorbance for solutions **L** to **P** now at λ_{max}. Don't disturb the filter in between.
4. **Now measure the absorbance for an unknown sample provided to you.**
5. Plot absorbance vs. concentration for samples **L** to **P**. Connecting maximum points, draw a straight line ideally passing through origin.
6. Using absorbance value for the unknown, find out its concentration.

OBSERVATIONS

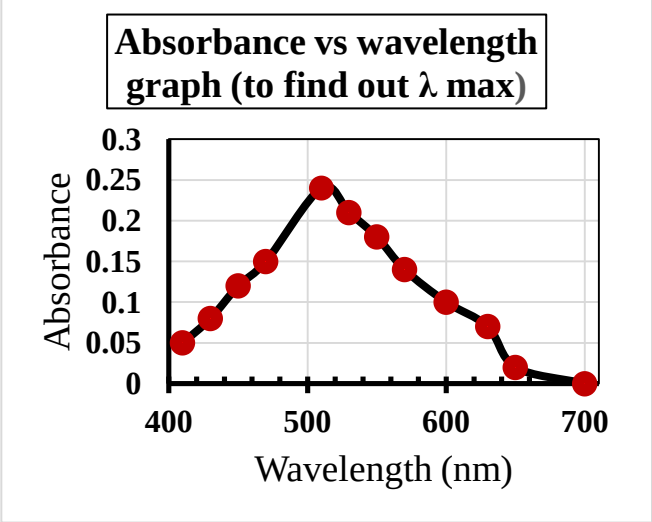
(i) Absorbance of the solution at highest concentration (10 $\times 10^{-5}$ N) at various λ

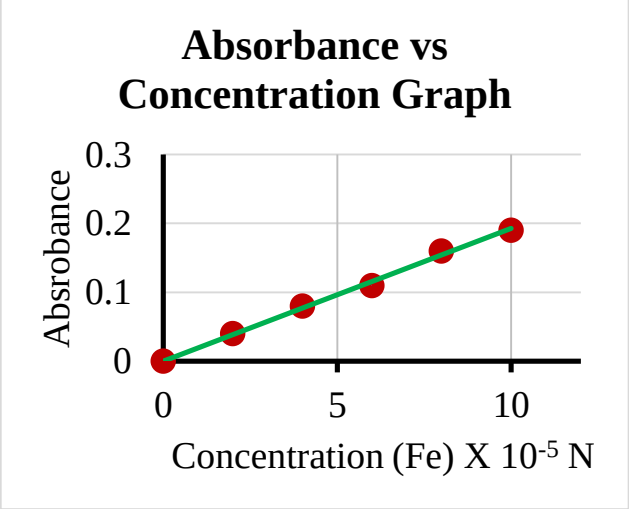
Wavelength (nm)	Absorbance

(ii) Absorbance of the solutions at different concentrations at λ_{max}

Concentration (N)	Absorbance

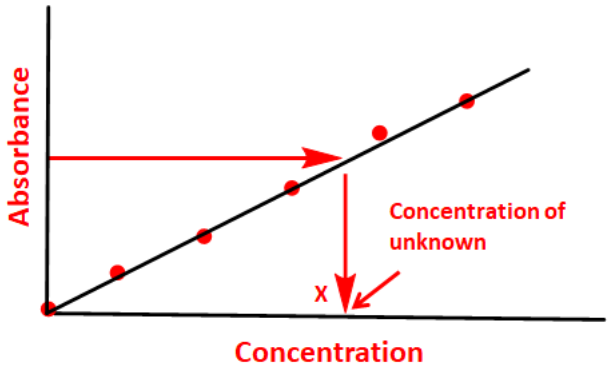
Sample UV-Vis and calibration curve (for the determination of concentration of unknown)





The concentration of unknown (**X**) can be determined from its absorbance value from the graph

A solution with Fe concentration of 2.00×10^{-5} N contains 10.00 µg of Fe (as used in this experiment). Hence knowing the Fe concentration of unknown samples, their Fe content in µg can be calculated.



RESULT: The Fe content in the unknown / given sample is _____ µg of Fe

Expected CLOs/Daily life application: Using colorimeter, the quantification of various metal ions, ligands can be done. It can also be used to extract the value of binding constant. Kinetics of a reaction can be measured in the colorimeter.

EXPERIMENT NO. 10

EXPERIMENT: To titrate potentiometrically ferrous ammonium sulphate solution against potassium permanganate and to determine the standard electrode potential of ferrous-ferric system.

APPARATUS: Pipette, burette, beaker, funnel, burette stand, clamp, potentiometer, calomel electrode (or Ag/AgCl electrode) and platinum electrode.

CHEMICALS: Mohr's salt solution (Ferrous ammonium sulfate; $FeSO_4(NH_4)_2SO_4.6H_2O$), potassium permanganate ($KMnO_4$) and sulphuric acid (H_2SO_4).

THEORY: An electrochemical cell is a device which establishes measurable electrical potential differences and in which flow of electrical current is accompanied by an overall chemical change. A reversible cell is that in which the overall chemical reaction can be reversed in the presence of an opposing external electromotive force of magnitude greater than that if cell itself. An electromotive cell consists of two electrodes or half cells, whose electrolytic solutions are either directly in contact with each other or connected through an intervening electrolytic solution. The net chemical change takes place at the individual electrodes; one of which is oxidation and the other reduction.

At the reversible electrodes, the oxidized and reduced states of a system exist in equilibrium in the solution, where an inert metal electrode (like Pt) is dipped into it e.g., Fe^{3+}/Fe^{2+}, in which the reaction is:

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$

The experimental cell:

$$Hg, Hg_2Cl_2(s)/KCl(saturated) \parallel Fe^{3+}/Fe^{2+}/Pt \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The e.m.f. of the cell:

$$E = E^0_{(Fe^{3+}/Fe^{2+})} + \frac{2.303\,RT}{nF}\log\frac{[Fe^{3+}]}{[Fe^{2+}]} - E_{(calomel)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Chemical reaction during potentiometric titration:

$$5\,Fe^{2+}_{(aq)} + MnO_4^-{}_{(aq)} + 8\,H^+ \longrightarrow 5\,Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)} + 4\,H_2O_{(l)}$$

When potassium permanganate solution is added to Mohr's salt solution, the concentration of Fe^{2+} ions decreases and that of Fe^{3+} ions increases, and as a result the emf of the cell increases

slowly. Near to the equivalence point, an inflection in seen due to fall in concentration of Fe^{2+} ions ultimately to 0, resulting in sudden rise in emf of the cell.

At half equivalence, eq. 2 becomes

$$E_{(\text{half equivalence})} = E^{o}_{(Fe^{3+}/Fe^{2+})} - E_{(\text{calomel})}$$

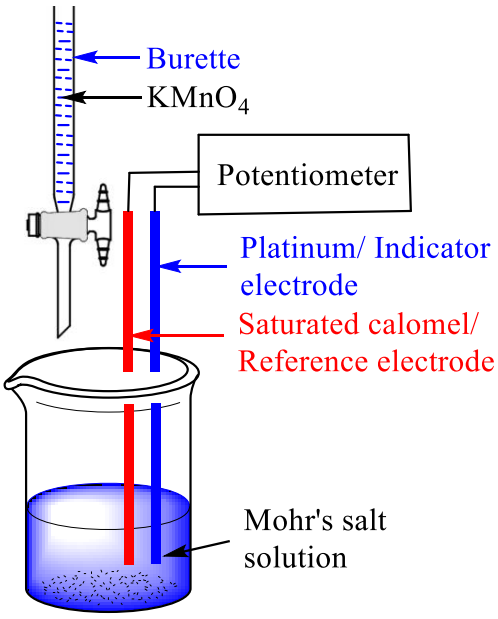
$$= E^{o}_{(Fe^{3+}/Fe^{2+})} - 0.242 \text{ (at 298 K)}$$

$$\therefore\ E^{o}_{(Fe^{3+}/Fe^{2+})} = E_{(\text{half equivalence})} + 0.242 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ (3)$$

Thus, by noting $E_{(\text{half equivalence})}$ from the graph, $E^{o}_{(Fe^{3+}/Fe^{2+})}$ can be calculated using eq. 3.

PROCEDURE

1. Take 50 ml of 0.1 N FAS solution in the beaker and add 5 ml of 1N sulphuric acid. Dip the platinum and saturated calomel electrodes in the solution.
2. Connect the indicator and the reference electrodes to the black and red terminals of the potentiometer, respectively.
3. Rinse and fill the burette with $KMnO_4$ (0.2 N).
4. Note the initial emf of the cell and start addition of the titrant ($KMnO_4$) in portions of 1 mL each. Near the equivalence point, decrease the volume of additional titrant to 0.5 ml and later on to 0.2 ml and note down to reading after each addition.
5. Continue to take 10-12 readings more, after a sharp change/increase in emf is noticed.



6. Plot emf (in volts) against the volume of $KMnO_4$ solution added (mL) and note down the equivalence point and the potential at half the equivalence point.

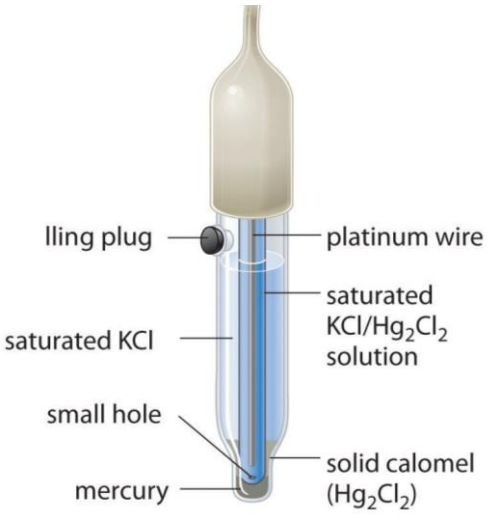
OBSERVATIONS

(i) Vol. of $KMnO_4$ Vs. e.m.f. of the solution

Vol. of $KMnO_4$ added from burette (mL)	e.m.f. (V)

Draw a graph EMF vs. Volumes of $KMnO_4$ (sample graph is as shown). Find out A [$E_{(half\ equivalence)}$] from the graph as under:

Vol. of $KMnO_4$ (mL) at equivalence point	**Vol. of $KMnO_4$ (mL) at half equivalence**	$E_{(half\ equivalence)}$ **($E_{1/2}$)**
X (along x-axis)	X/2 (along x-axis)	**A** (along y-axis)



Saturated calomel electrode (Reference electrode)

Platinum electrode

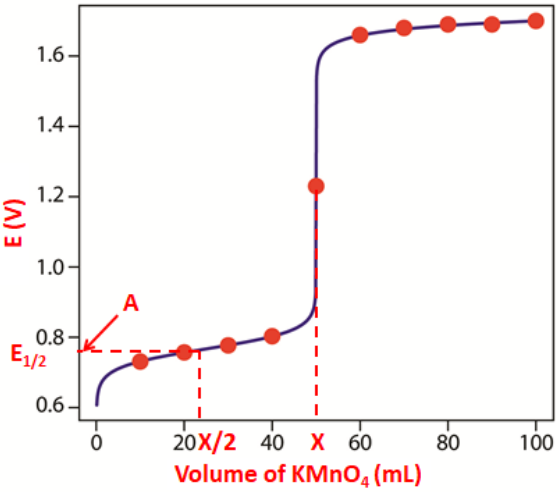
GENERAL CALCULATIONS

The e.m.f. at half-equivalence point (**A**) is observed from graph.

$$E_{(half\ equivalence)} = E^o_{(Fe^{3+}/Fe^{2+})} - E_{(calomel)}$$

$$E^o_{(Fe^{3+}/Fe^{2+})} = E_{(half\ equivalence)} + E_{(calomel)}$$

$$E^o_{(Fe^{3+}/Fe^{2+})} = \mathbf{A} + 0.242 = \_\_\_\_\_\ V$$



RESULT: The standard half-cell potential of Fe^{3+}/Fe^{2+} couple is _____ V.

PRECATIONS

1. After each addition of the titrant/ $KMnO_4$, the contents of the beaker should be stirred gently.
2. Electrodes should be handled very carefully.

Expected CLOs/Daily life application: To quantify alkalinity, acid content, and chloride ion, fluoride ion and various other ions in water, fertilizers, soil etc. Solubility product (K_{sp}) of salts can also be determined using potentiometry.

EXPERIMENT NO. 11

EXPERIMENT: To determine the total cation concentration in natural water

APPARATUS: Ion-exchange column of 10cm length, burette, pipette etc.

CHEMICALS: NaOH, HCl

THEORY: Ion exchange resins are solid polymeric materials with fixed positive (or negative) charges that can be exchanged with the mobile cations (or anions). This process is reversible and electro-neutrality is maintained in both the mobile liquid-phase and the fixed solid-phase. These resins are used for water softening and deionization.

When water is passed through a chromatographic column packed with a cation-exchange resin in H^+ form (H^+ ion as counter ion), the cations in water (Ca^{2+}/ Mg^{2+}) are exchanged with H^+ ions of the resin. The liberated H^+ ions are estimated by titration against standard alkali solution.

The alkalinity in water sample (due to the presence of carbonates, bicarbonates etc.) can be determined by titration with standard HCl and is to be taken care for the total cation exchange.

$$CO_3^{2-} + 2H^+ \longrightarrow CO_2 + H_2O$$

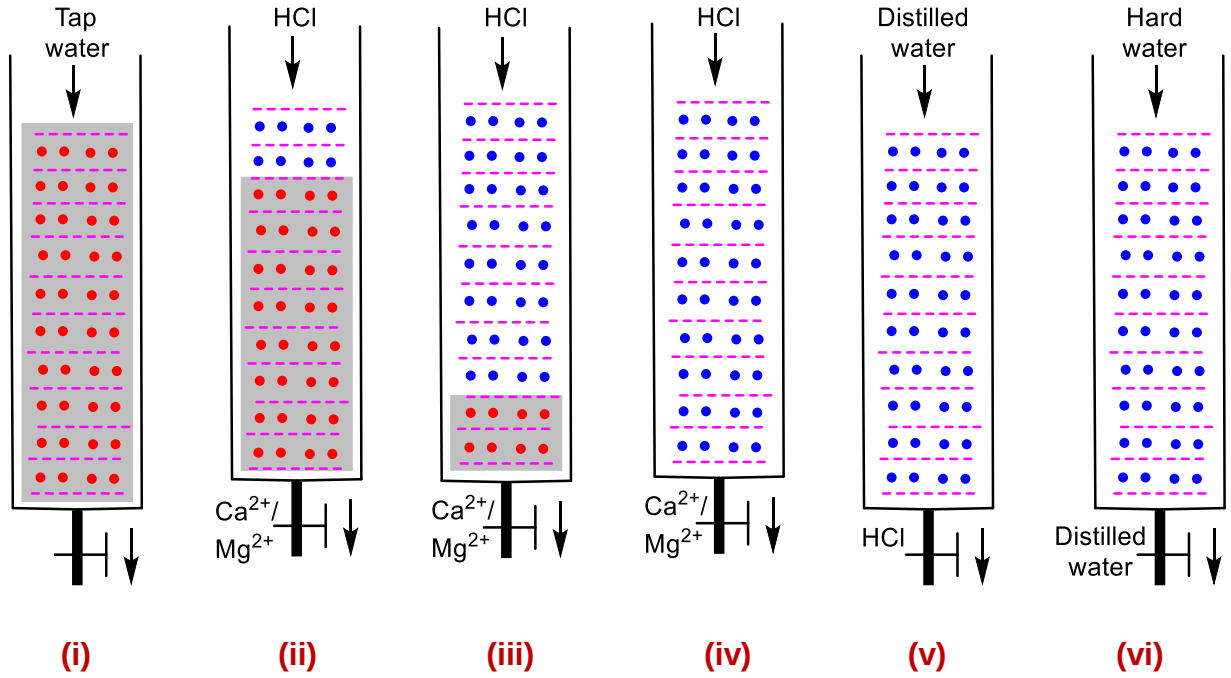
$$HCO_3^- + H^+ \longrightarrow CO_2 + H_2O$$

In water analysis, it is conventional to express the total cation concentrations as parts per million (ppm) of $CaCO_3$ per dm^3 of water. This unit is also called the equivalent mineral acidity (EMA).

PROCEDURE: Prepare and standardize a 0.02 N sodium hydroxide (carbonate free) solution in the usual manner.

(A) Regeneration of exhausted (cation-exchange) resin: Prepare a 10 cm column of a suitable cation-exchange resin in a 15 – 18 nm wide chromatographic tube. Pass very slowly (2 – 3 mL per minute) about 25 mL of 2N HCl through the column (in about 15 minutes) to convert the resin to H^+ ion form. Rinse the column with 50 mL distilled water to remove interstitial /excess of HCl. Rinsing may be continued till 10 mL of the effluent does not require more than one drop of 0.02 N NaOH to give alkaline test with phenolphthalein as indicator.

Scheme A: <u>Regeneration of exhausted (cation-exchange) resin</u>



(i) Column with exhausted resin (Ca^{2+} / Mg^{2+} ion form); Pass tap water through the column to remove any interstitial air-pockets / gaps.
(ii), (iii) and (iv) Regenerate the exhausted resin with dil. HCl. **(iv)** is the resin in H^+ ion form.
(v) Pass distilled water through the column to displace HCl present in the interstitial space.
(vi) Pass hard / tap water (~ 50 mL) through the column to displace distilled water in the column and **discard the effluent**.

● Regenrated resin (H^+ ion form)
● Exhausted resin (Ca^{2+} / Mg^{2+} ion form)

(B) <u>Determination of total cation concentration of hard water</u>: Pass about 50 ml of the test water (tap water sample) through the column at a rate of 3 – 4 mL per minute in order to displace the distilled water (present in interstitial space) and discard the effluent.

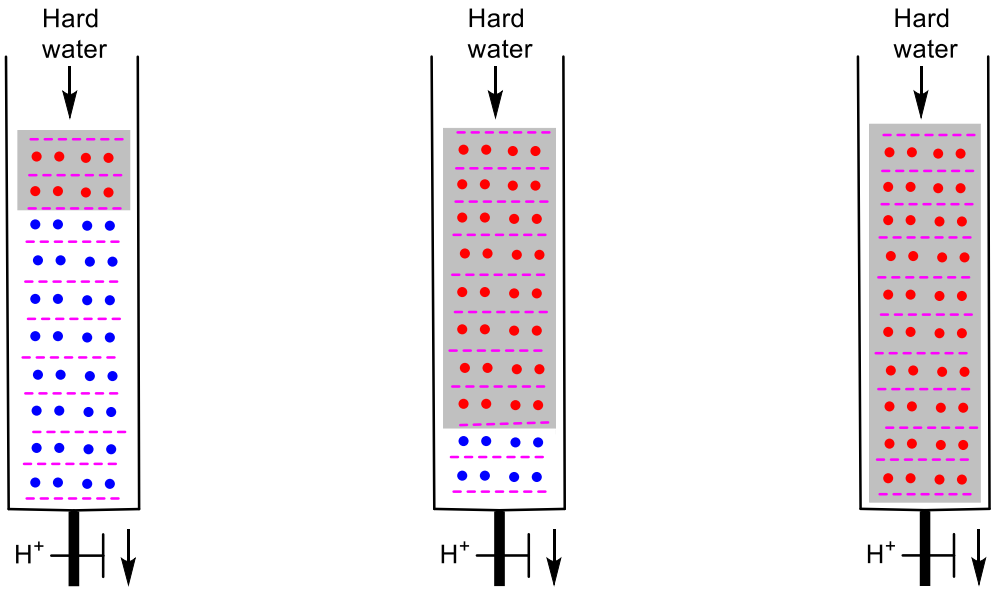
Once again pass about 120 mL of the test water (tap water sample) through the column at the same rate and collect it in a beaker / titration flask.

Pipette out 25 mL of the effluent into another conical flask and titrate it against 0.02 N NaOH taken in the burette. Repeat this step for 3 more times.

If the test water is alkaline, as many commercial water samples are, due to the presence of carbonates, bicarbonates etc., the alkalinity is to be determined by titration of 100 mL of the

sample against a 0.04 N HCl using methyl orange as indicator. This alkalinity is to be corrected for in the calculation of the equivalent mineral acidity of the sample.

Scheme B: <u>Determination of total cation concentration of hard water</u>



(vii) **(viii)** **(ix)**

(vii) & (viii) Continue passing another ~ 120 mL of hard / tap water through the column; Ca^{2+} / Mg^{2+} of water will be exchanged with H^+ ions of the resin; collect the (acidic) effluent for analysis/ titration.
(ix) Exhausted resin (Ca^{2+} / Mg^{2+} ion form). Repeat steps **(i) – (vi)** to regenerate the resin.

● Regenrated resin (H^+ ion form)
● Exhausted resin (Ca^{2+} / Mg^{2+} ion form)

<u>OBSERVATIONS</u>

(i) Cation concentration of test water sample

Volume of effluent taken for each titration = 25 mL

Sr. No.	Burette reading (mL)		Volume of NaOH used (mL)
	Initial	Final	
1.			
2.			
3.			
4.			

Mean volume of HCl used (V_1) = _____ (mL)

(ii) Alkalinity of test water sample:

Volume of test water sample taken for each titration = 100 mL

Sr. No.	Burette reading (mL)		Volume of HCl used (mL)
	Initial	Final	
1.			
2.			
3			
4.			

Mean volume of HCl used (V_2) = _____ (mL)

CALCULATIONS: Concentration of NaOH solution used for titration = a N

Volume of aliquot used for titration = 25 ml

Volume of NaOH used for neutralizing 25 ml of the aliquot = V_1 ml

Equivalent mineral acidity of the sample = (aV x 50 x 1000)/25 = 2000 aV ppm of $CaCO_3$

The following correction term has to be added to the result if the original test sample shows alkaline reaction to methyl orange indicator.

Correction term = $500bV_2$ ppm of $CaCO_3$

Where b = normality of HCl solution used for titration

V_2 = volume in ml of HCl solution neutralizing 100 ml of the test water sample.

RESULT:

Equivalent mineral acidity (Uncorrected) = _____ ppm of $CaCO_3$

Alkalinity (Correction factor) = _____ ppm of $CaCO_3$

Equivalent mineral acidity (Corrected) = _____ ppm of $CaCO_3$

Expected CLOs/Daily life application: Ion exchange is most often used in water-softening and other purification and separation processes. It has become more popular as more and more homes acquire water softeners to remove Ca^{2+} and Mg^{2+} from water.

EXPERIMENT NO. 12

EXPERIMENT: Determination of cloud and pour point of given oil sample

APPARATUS: Cloud and pour point apparatus, thermometer and ice cubes.

CHEMICALS: Coconut oil, Petroleum

THEORY: 'Cloud point' and 'Pour point' are the two parameters which determine the quality of oil. Cloud point parameter is limited to only oils which are transparent. Lubricating oils obtained from petroleum usually contains paraffin wax and other asphaltics impurities, their amount depending upon the efficiency of refining and de-waxing processes. When petroleum is chilled under specific conditions, the temperature at which paraffin wax or other solidifiable materials (normally dissolved in oil) begin to separate out from solution in the form of minute crystals, causing the oil to become less transparent, cloudy or hazy in appearance is known as the cloud point of the oil. If the cooling is continued further, the amount of separating oil increases and a stage is reached at which the oil solidifies and stops flowing. The lowest temperature at which the oil will not flow or pour under the prescribed conditions, when cooled undisturbed at a fixed rate is called its pour point.

PROCEDURE

(A) Determination of Cloud Point

(i) Bring the oil sample to be tested to a temperature at least 15 ^{o}C above the expected cloud point. If the sample contains moisture, dry it by shaking with a little anhydrous sodium sulphate followed by filtration.

(ii) Pour the clear oil into test jar upto etched mark.

(iii) Tightly close the jar with a cork carrying thermometer with a bulb touching the bottom of the jar.

(iv) Insert the test jar inside a holding jacket (made of glass or copper), which is immersed in freezing mixture suitable for obtaining the desired temperature.

(v) After every 2 ^{o}C fall in temperature of oil, take the oil sample out of the test jar from the jacket. Inspect the cloudiness and immediately replace it in the jacket.

(vi) Record the temperature of such inspection at which it first reveals a distinct cloudiness in oil sample near to the bottom of jar and report it as the cloud point.

(B) Determination of Pour Point

(i) The same procedure as above is followed for cooling the oil except that the thermometer bulb is just completely immersed in the oil.

(ii) Take out the test jar after every 3 ^{o}C fall in temperature and tilt it just enough to see any movement of oil. Immediately replace the jar in jacket.

(iii) A point (temperature) at which oil does not show any movement in jar on tilting and holding the jar in horizontal position for 5 seconds.

(iv) Record the reading on the test thermometer as solid point.

(v) Add 3 ^{o}C to this temperature and report that as pour point.

OBSERVATIONS

Cloud point = _____ ^{o}C

Solid point = _____ ^{o}C

Pour point = Solid point + 3 ^{o}C

RESULTS

Cloud Point = _____ ^{o}C

Pour point = Solid point + 3 ^{o}C

PRECATIONS

(1) The test jar should not touch the jacket. This is achieved by placing a cork disk at the bottom of jacket and using a gasket around the test jar.

(2) The complete operation, removal and replacement of test jar should not take more than 3 seconds.

(3) After the cloud point reaches, the mass of oil should not be disturbed as this may result in delay solidification and so lower value of the result will be obtained.

Expected CLOs/Daily life application: Cloud point helps to determine the minimum operating temperature of an automobile etc.

Hope you enjoyed the Laboratory Experiments of Applied Chemistry (UCB008) Course

All The Best!