# B.Sc. CHEMISTRY LAB MANUAL

2nd Semester

Prepared By

**Pure & Applied Science Dept.**

Chemistry

## MIDNAPORE CITY COLLEGE

**MIDNAPORE CITY COLLEGE**

***Department of Pure and Applied Sciences***

**B.Sc. in Chemistry**

**Semester: II**

**Course contents:**

**Paper Code: CEMHMJ102**

**Acid and Base Titrations:**

1. Estimation of carbonate and hydroxide present together in mixture

2. Estimation of carbonate and bicarbonate present together in a mixture.

3. Estimation of free alkali present in different soaps/detergents.

**Oxidation-Reduction Titrimetric**

1. Estimation of Fe(II) using standardized KMnO4 solution

2. Estimation of oxalic acid and sodium oxalate in a given mixture

3. Estimation of Fe(II) and Fe(III) in a given mixture using $K_2Cr_2O_7$ solution.

4. Estimation of Fe(III) and Mn(II) in a mixture using standardized $KMnO_4$ solution.

5. Estimation of Fe(III) and Cu(II) in a mixture using $K_2Cr_2O_7$

6. Estimation of Fe(III) and Cr(III) in a mixture using $K_2Cr_2O_7$

**Paper Code: CEMSEC02P**

**Part-A: Extraction**

i) Extraction of eucalyptus leaf ingredient

ii) Extraction of eugenol from clove

iii) Extraction of nicotine from tobacco

iv) Curumine from turmeric

v) Extraction of caffeine from tea/coffee

**Paper Code: CEMMI02P**

**MI2P: Organic Chemistry- LAB**

Qualitative Analysis of Single Solid Organic Compound(s)

Experiment A: Detection of special elements (N, Cl, and S) in organic compounds.

Experiment B: Solubility and Classification (solvents: $H_2O$, dil. HCl, dil. NaOH)

Experiment C: Detection of functional groups: Aromatic-$NO_2$, Aromatic -$NH_2$, - COOH, carbonyl (no distinction of –CHO and >C=O needed), -OH (phenolic) in solid organic compounds.

Experiments A - C with unknown (at least 6) solid samples containing not more than two of the above type of functional groups should be done.

**Physical Chemistry-LAB**

(I) Study the kinetics of the following reactions

a) Initial rate method: Iodide-persulphate reaction

b) Integrated rate method:

(i) Acid hydrolysis of methyl acetate with hydrochloric acid

(ii) Compare the strengths of HCl and $H_2SO_4$ by studying kinetics of hydrolysis of methyl acetate

(iii) Decomposition of $H_2O_2$

**Paper Code: CEMHMJ102**

## Acid and Base Titrations

Acid-base reactions are of great practical importance in analysis, not only because of their usein titrating a large number of inorganic and organic substances, but also because the hydrogenionconcentrationofa solutionoftenisofgreatimportance incontrollingreactions.

**Titration:**

Theprocessofdeterminingthevolumeofagivensolutionofareagentequivalenttotheamountofanotherreactantpresentinastandardsolutionisknownas titration.

**Equivalent WeightofAcidsandBases:**

The equivalent weight of an acid is that weight which yields one mole of hydrogen ions in thereaction employed whereas the equivalent weight of a base is that weight which reacts withone moleofhydrogenions inthereaction.

**Normalsolution:**

Asolution containingoneequivalent weightofsoluteperlitreofsolution.

**EquivalencePoint:**

When the number of equivalents of acid (respectively base) added is equal to the number ofequivalentsofbase(respectivelyacid) takeninitially,wehavereachedtheequivalencepoint.

**Acid-BaseIndicators:**

Weak organic acids or bases having different colours for their dissociated or undissociatedformse.g.,phenolredwhichisyellowincolourinitsundissociatedforminacidicsolutionandredinits dissociatedforminbasic solutionconstitutethese indicators.

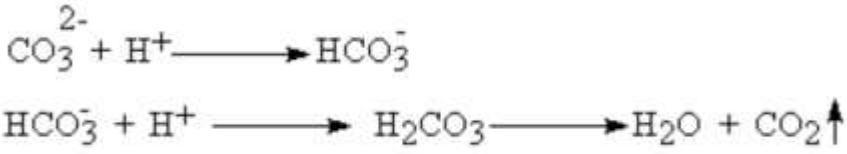
| Name ofindicator | Colour in acidsolution | Colourinbasic solution | pHrange |
|---|---|---|---|
| Methyl Orange | Red | Orange –yellow | 3.1–4.6 |
| Bromophenol Blue | Yellow | Blue –violet | 3.0–4.6 |
| MethylRed | Red | Yellow | 4.2–6.3 |
| Bromothymol Blue | Yellow | Blue | 6.0–7.6 |

| | | | |
|---|---|---|---|
| ThymolBlue | Yellow | Blue | 8.0–9.6 |
| Phenolphthalein | Colourless | Red | 8.0–9.8 |
| Thymolphthalein | Colourless | Blue | 9.4–10.6 |

**Experiment 1: Estimation of carbonate and hydroxide present together in mixture**

**Theory:**

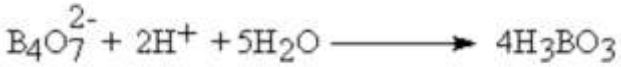
Carbonateion reactswith hydrogen ionsinsteps:



The pKa1 and pKa2 values of H2CO3 are quite distinct and so when a carbonate solution istitrated against hydrochloric acid, there occur two distinct regions of sharp pH change. Thefirst corresponding to the formation of HCO (pH 8 to 10) and the second due to completeneutralizationatpH4-6.ThefirstisroughlyinthepHrangeinwhichcolourofphenolphthaleinchanges from red to colourless and the second is that at which methyl orange changes fromyellow to orange red. This end point, however, is not very sharp in the titration of the strongbase NaOH. The sharp change of pH occurs over a range of pH that includes the regions ofcolourchange ofboththeindicators, sobothofthemgive theendpointcorrectly.

When we have both sodium carbonate and sodium hydroxide present together in a solution, atitration using phenolphthalein gives the titre (volume at the equivalence point)
correspondingtosodiumhydroxideplushalfthecarbonateandthetitreobtainedwithmethylorangecorresponds to the total alkali. The individual sodium carbonate and hydroxide concentrationsmaybecalculatedfromthe data.

The HCl solution used may be standardized by titration with a standard solution of sodiumtetraborate decahydrate (borax) or anhydrous sodium carbonate. The reaction



involved in thecase ofboraxis

Borax ispreferableasaprimarystandardbecauseofitshigherequivalent weight.

**Procedure:**

Prepare 100 mL of a standard solution of $Na_2B_4O_7 .10H_2O$ (approximately N/20) by weighingaccurately about one gram of borax, dissolving it in distilled water and making up to 100 mL.Titrate 10 mL portion of this solution against the supplied hydrochloric acid till concordanttitres are obtained, using 2 drops of methyl orange as indicator. Calculate the strength of theHClsolution.

Pipette out 10 mL solution of a mixture of sodium carbonate and sodium hydroxide into aconical flask, add two drops of methyl orange indicator and titrate against HCl, till the colourchanges from pale yellow to orange. Note the titre value ($V_1$). Titrate 10 mL portions of thesolutionusingphenolphthaleinasindicator(1-2drops).Thecolorchangeshereattheendpointis from red to colourless and is quite sharp. Let the titre be $V_2$ of HCl. Therefore, $2(V_1 - V_2)$corresponds to carbonate, and $V_1 – 2(V_1– V_2) = 2V_2– V_1$ corresponds to sodium hydroxide.Calculatethe amount of$NaOH$and $Na_2CO_3$presentin alitreofthe givensolutioning/L.

**Experiment2:Estimationofcarbonateandbicarbonatepresenttogetherinamixture.**

Thisprocedureinvolvestwotitrations.First,totalalkalinity(=$[HCO_3^-]$+2$[CO_3^{2-}]$)ismeasured bytitratingthe mixturewithstandardHCltoabromocresolgreenendpoint:

$$HCO_3^- + H^+ \rightarrow H_2CO_3$$
$$CO_3^{2-} + 2H^+ \rightarrow H_2CO_3$$

A separate aliquot of unknown is treated with excess standard NaOH to convert

$HCO_3^-$ to$CO_3^{2-}$:

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$

Then all thecarbonateisprecipitatedwith $BaCl_2$:

$$Ba^{2+} + CO^{2-}{}_3 \rightarrow BaCO_3$$

The excess NaOH is immediately titrated with standard HCl to determine how much $HCO_3^-$ was present. From the total alkalinity and bicarbonate concentration, you can calculate the original carbonate concentration.

**Reagents**

Standard 0.1 M NaOH and standard 0.1 M HCl:

$CO_2$-free water: Boil 500 mL of distilled water to expel $CO_2$ and pour the water into a 500-mL plastic bottle. Screw the cap on tightly and allow the water to cool to room temperature. Keep tightly capped when not in use. 10 wt% aqueous $BaCl_2$: 35 mL/student. Bromocresol green and phenolphthalein indicators.

Unknowns: Solid unknowns (2.5 g/student) can be prepared from reagent-grade sodium carbonate or potassium carbonate and bicarbonate. Unknowns should be stored in a desiccator and should not be heated. Heating at 50°–100°C converts $NaHCO_3$ to $Na_2CO_3$.

**Procedure:**

**1.** Accurately weigh 2.0–2.5 g of unknown into a 250-mL volumetric flask by weighing the sample in a capped weighing bottle, delivering some to a funnel in the volumetric flask, and reweighing the bottle. Continue this process until the desired mass of reagent has been transferred to the funnel. Rinse the funnel repeatedly with small portions of $CO_2$-free water to dissolve the sample. Remove the funnel, dilute to the mark, and mix well.

**2.** *Total alkalinity:* Pipet a 25.00-mL aliquot of unknown solution into a 250-mL flask and titrate with standard 0.1 M HCl, using bromocresol green indicator standardizing HCl. Repeat this procedure with two more 25.00-mL aliquots.

**3.** *Bicarbonate content:* Pipet 25.00 mL of unknown and 50.00 mL of standard 0.1 M NaOH into a 250-mL flask. Swirl and add 10 mL of 10 wt% $BaCl_2$, using a graduated cylinder. Swirl again to precipitate $BaCO_3$, add 2 drops of phenolphthalein indicator, and immediately titrate with standard 0.1 M HCl. Repeat this procedure with two more 25.00-mL samples of unknown.

**4.** From the results of step 2, calculate the total alkalinity and its standard deviation. From the results of step 3, calculate the bicarbonate concentration and its standard deviation. Using the standard deviations as estimates of uncertainty, calculate the concentration (and uncertainty) of carbonate in the sample. Express the composition of

the solid unknown in a form such as$63.4(\pm0.5)wt\%K_2CO_3$and$36.6(\pm0.2)wt\%NaHCO_3$.

**Experiment 3:Estimationoffreealkalipresentin different soaps/detergents.**

Theusualmethodofmakingthisdeterminationprescribesaseparationofcausticfromcarbonated alkali by drying the soap, dissolving in absolute alcohol, and after filtering andwashingtheundissolvedcarbonatewithalcoholanddissolving inwatertotitratethesolutionscontaining caustic and carbonate, respectively, with standard acid. This method is open toseveral

objections, aside from the amount of time consumed. If it is desired to obtain accurate resultson the caustic and carbonate separately, the preliminary drying of the soap introduces an errorsincethecausticalkaliwilltakeupcarbondioxidefromtheairunlessthedryingisdoneout of contact with air. It is quite a troublesome process to filter an alcoholic soap solution if oneisnot provided withappliancesto keepthe funnelhot duringfiltration.Dudleyand Pease'usean alcoholic solution of stearic acid for titrating the caustic, but still filter from undissolvedcarbonate,anddeterminethelatterintheusualmanner.Inthefollowingprocessthe writerhassucceededineliminatingfiltration.

Forthismethoditisnecessary to providethreestandardsolutions:

1.Hydrochloric acid,N/10(forstandardizing2).

2 .Caustic soda,N/10,in alcohol.

3. Stearicacid,N/10,in alcohol.

2 and 3 should be exactly equivalent one to the other, titrated warm with phenolphthaleinindicator.Twogramssoap(whichneedsnodrying)isweighedintoaround-bottomedflask,ofabout300cc.capacity,and50 cc.alcohol pouredupon it.N/10stearicacidisnowruninfroma burette in amount judged to be sufficient to neutralize the free alkali in 2 grams of the soap,some phenolphthalein added, and the flask then stoppered with a cork stopper, through whichpasses a glass tube about 30 inches long and of about inch internal diameter, the lower endground to a point on a giindstone, and the purpose of which is to serve as areflux condenser.The flask and

contents are placed on a steam-bath and heated thirty minutes, at the expirationof which time the solution should be quite clear and show no alkali with the phenolphthalein.Ifthesolutionturnsredduringtheboiling,showingthataninsufficientquantityofstearicacidhasbeexiaddedatfirst,addmoreofthatsolutionuntilthecolordisappears,thenseveralcubiccentimetersinexcess,andheattwentyminutesfurther.Theflaskisnowremovedfromthebathand, after a few minutes' cooling, titrated with N/10 caustic soda. The difference between thenumber of cubic centimeters stearic acid solution added and the number of cubic Centimeterscaustic soda used to back titrate is equivalent to the total free alkali present. While the firstflaskisheating,weighoutinsimilarflask2gramsofsoapandadd50cc.alcoholandplaceonthe steanibath. When the first test is finished, calculate roughly the total alkali, assuming thetotal quantity to be carbonate. Now add to the second flask an amount of 10 per cent. bariumchloridesolutionsufficienttoprecipitatealkalifound,'heatafewminutes,addphenolphthalein, and titrate with N/10 stearic acid. Thebtitration must take place slowly andwiththoroughagitationofbtheliquidforthereasonthatthesodiumorpotassiumhydroxide breacts with the barium chloride added and forms sodium chloride band bariumhydroxide.Thelatterisnotverysolubleinthealcoholicliquidandsufficienttimeandpains must be taken to ensure its complete neutralization by the stearic acid. **A** blank test should bemade on 50 cc. of the alcohol, since this frequently contains carbon dioxide, and the numberof tenths cc. N/10 caustic soda necessary to neutralize the free acid in this quantity of alcoholadded to the reading of the stearic acid burette in the second test. This corrected reading givesthe number of cubic centimeters N/10 stearic acid used to neutralize the caustic alkali in 2grams of soap. The difference between the total alkali found and the caustic will, of course,give thecarbonate.

Forexample:2gramsofsoapand15cc.N/10stearic acid;runin3.2cc.N/IOcaustic sodatobacktitrate.Consequently, 15 −3.2 =11.8 cc.N/10stearicacid equivalent tototalfreealkali.

Toneutralizethecausticinthesampletreatedwithbariumchloridewasrequired4.1cc.N/10stearic acid. 50 cc. of the alcohol used required 0.2 cc. N/10 caustic soda, then 4.1 + 0.2 = 4.3cc.N/10stearicacidtoneutralizefreecaustic alkali.

11.8 − 4.3 =7.5cc N/10stearic acidto neutralize carbonatedalkali.

Icc.N/10stearic acid =0.004gram caustic sodaor0.0053gramsodiumcarbonate.

I cc. N/10 stearic acid = 0.0122 gram$BaCl_2.2H_2O$ or 0.122 cc. 10 per cent. Barium cholride$_{solution}$.

The above figures calculated to percentage would be : 0.86 per cent. caustic soda and 1.99 percent. sodium carbonate. It is to be noted that a rubber stopper cannot be used in the flasks fordissolving the soap on account of the sulphur in the rubber, which decolorizes an alcoholicsolution of phenolphthalein. The niethod is applicable to all soaps which do not contain fillerswhichreactwiththestandardsolutionsemployed.

## Experiment 4: Estimation of Fe(II) using standardized $KMnO_4$ solution.

**Theory:**

The reaction between Mohr's salt solution and potassium permanganate solution in acidmedium is oxidation–reduction or redox reaction where potassium permanganate solution isthe oxidizingagentandMohr'ssaltsolutionis thereducingagent.

**Reaction:**

$$MnO^{4-} + 8H^{+} + 5e = Mn^{+2} + 4H_2O$$
$$5Fe^{+2} = 5Fe^{+3} + 5e$$

$$MnO^{4-} + 5Fe^{+2} + 8H^{+} = 5Fe^{+3} + Mn^{+2} + 4H_2O$$

**Procedure:**

Preparationof100ml(N\10)standard oxalicacid solution.

Equivalent weightofoxalicacid =63

1000ml of 1(N) oxalic acid solution contain 63gm oxalic acid.Hence100 ml (N/10)oxalicacidcontain 0.63 gmoxalicacid.

About 0.63gm of oxalic acid is weighed from a weighing bottle by difference and is pouredinto 100ml volumetric flask, dissolved in small volume of water by shaking and the volume ismade uptothemarkwithdistilledwaterandthoroughlyshaken.

Therefore,Strength =x/0.63(N\10)=$S_1$(N).

**Standardizationofgivenpermanganatesolutionagainststandardoxalicacidsolution.**

ThereactionbetweenKMnO4andoxalicacid isanexampleofredox reaction.HereacidifiedKMnO4actsas anoxidizingreagentwhileoxalicacidis a reducingagent.

**Reaction:**

$2KMnO_4+3H_2SO_4=K_2SO_4+2MnSO_4+3H_2O+5[O]$

$5COOH\text{-}COOH+5[O]=10CO_2+5H_2O$

**TitrationofgivenKMnO4solutionwithstandardoxalicacidsolution**

10 ml of standard oxalic solution are pipetted into a 250ml conical flask. Now 10 ml of (1:4)$H_2SO_4$solution is added, the solution is warmed to 60 - 700 C and then titrated with thepermanganate solution from the burette till first permanganate pink color is seen. And theprocessis repeatedtwice.

**4. EstimationofFe$^{2+}$ inMohr'ssalt.**

5ml of Mohr's salt solution is pipetted out into a 250ml conical flask. Now 2 ml of $H_2SO_4$and$H_3PO_4$ (1:4) and 20ml of distilled water is added to the solution. The solution is titrated withstandardKMnO4solutiontillthefirstpermanentpinkcolorisseen.

**RESULT:**

**1. Recording of temperature:**

| Initial temperature($^0$c) | Final temperature($^0$c) | Mean temperature($^0$c) |
|---|---|---|
| | | |

**2. Preparation of 100 ml (N/10) Oxalic Acid solution**

| Weight taken (gm) | Weight to be taken (gm) | Strength (N) |
|---|---|---|
| | 0.63 | |

**3.Table: Titration of oxalic acid with $KMnO_4$**

| Sl.no. | Vol. of oxalic Acid (ml) | Strength of oxalic Acid (N) | Burette reading of $KMnO_4$ (ml) | | | Mean vol. of $KMnO_4$ (ml) |
|---|---|---|---|---|---|---|
| | | | Initial (ml) | Final (ml) | Vol. required (ml) | |
| 1. | | | | | | |
| 2. | | | | | | |

**4.Table. Titration of Mohr's salt solution with $KMnO_4$:**

| Sl.no. | Vol. of Mohr's salt solution(ml) | Strength of $KMnO_4$ (N) | Burette reading of $KMnO_4$ (ml) | | | Mean vol. of $KMnO_4$ (ml) |
|---|---|---|---|---|---|---|
| | | | Initial (ml) | Final (ml) | Vol. required (ml) | |
| 1. | | | | | | |
| 2. | | | | | | |

**CALCULATION:**

**(A) StrengthofKMnO4solution:**

We know $V_1S_1 = V_2S_2$ or, $S_2 = V_1S_1/V_2$

= .....(N)

Here, $V_1$=volume of oxalic acid $S_1$= strengthofoxalic acid

$V_2$= volume of KMnO4 $S_2$=strengthofKMnO4

**(B) Strength of $Fe^{2+}$ in Mohr's salt solution:**

Volume of $KMnO_4$ solution required for Mohr's salt solution = **a**cc = ..... cc.

Strength of $KMnO_4$ solution = **y**(N) = ..... (N).

**a**ml of **y**(N) $KMnO_4$ solution ≡ 55.85 × **a** × **y**/1000 gm of $Fe^{2+}$

≡ z gm of $Fe^{2+}$ = ..... gm.

1000 ml of Mohr's salt contain = z X 1000/5 gm of $Fe^{2+}$

= ..... gm. = w gm of $Fe^{2+}$

Amount of $Fe^{2+}$ = wgm/lit = ..... gm./lit

**DISCUSSION:**

Estimation of $Fe^{+2}$ was done in the supplied Mohr's salt solution by redox titration using $KMnO_4$ as oxidizing agent. All the apparatus were well cleaned with distilled water prior to the experiment. If the apparatus are not cleaned properly, then sole determination of $Fe^{+2}$ in the Mohr's salt solution is not possible as water may contain trace amount of $Fe^{+2}$ ions. The standardization of $KMnO_4$ was done by heating oxalic acid solution at 60-70°C, redox titration will take place to a certain extent and strength of $KMnO_4$ will be of lower value. The mineral acid $H_2SO_4$ should be used in the reaction mixture as redox titration takes place under acidified condition. Mineral acid like HCl or $HNO_3$ should not be used as HCl reacts with $KMnO_4$ and $HNO_3$ itself is an oxidizing agent. The use of ($H_2SO_4$:$H_3PO_4$) in the Mohr's salt solution is to maintain the proper pH and $H_3PO_4$ reacts with $Fe^{+3}$ to form $FePO_4$ and complete oxidation of $Fe^{+2}$ proceeds and the equilibrium shifts to the right ($Fe^{+2}$ to $Fe^{+3}$). As redox reaction is temperature dependent, estimation of $Fe^{+2}$ is done at a fixed temperature i.e. room temperature.

**Conclusion:**

The amount of $Fe^{2+}$ estimated in the supplied Mohr's salt solution is…….. gms./lit at ..... $^0$C.

**Experiment5:Estimationofoxalicacidandsodiumoxalate ina givenmixture.**

**Theory:**

*Molecular Equations*

$$2\,KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$\begin{matrix}COOH\\|\\COOH\end{matrix} \cdot 2H_2O + [O] \longrightarrow 2CO_2 + 3H_2O$$

$$\begin{matrix}COONa\\|\\COONa\end{matrix} + H_2SO_4 + [O] \longrightarrow 2CO_2 + H_2O + Na_2SO_4$$

*Ionic Equations*

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O\ ] \times 2$$

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-\ ] \times 5$$

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

Both oxalic acid and sodium oxalate can be titrated against N/20 KMnO4 since both of themare reducingagents.

So normality (N/2) of the solution will be due to both of them. From the combined normality(N/2),thecompositionofeachcanbecalculated.

**Indicator**

KMnO4isaself-indicator.

**EndPoint**

Colourlessto permanent pink(KMnO4inburette).

**Procedure**

Rinseandfill theburette withthe N/20KMnO4,solution.

Weigh exactly 1.0 g of the given mixture of oxalic acid and sodium oxalate and dissolve inwater to prepare exactly 250 ml of solution using a 250 ml measuring flask. Rinse the pipettewith the preparedoxalatesolutionandpipette out20.0mlofitina washedtitrationflask.

Addonetest-tube(~20ml)fullofdilutesulphuricacid(~4N)tothesolutionintitrationflask.Note theinitialreadingoftheburette.

Heatthesolutionoftitrationflask to60-70°CandrundownKMnO4solution fromtheburettetill a permanentlightpinkcolourisjustimpartedtothe solutioninthe titrationflask.

Notethe finalreadingoftheburette.

Repeattheabovesteps4−5timesto getthreeconcordantreadings.

**Observations**

NormalityofKMnO4solution =1/20

Volumeofoxalatesolutiontaken foreach titration=20.0ml.

Calculations
x ml ofN/20KMnO4solution areequivalentto 20ml ofthegiven oxalatesolution.

| *S. No.* | *Initial reading of the burette* | *Final reading of the burette* | *Volume of the $KMnO_4$ solution used* |
|---|---|---|---|
| 1. | — | — | — ml |
| 2. | — | — | — ml |
| 3. | — | — | — ml |
| 4. | — | — | — ml |

Concordant volume = $x$ ml (say).

**Applyingnormalityequation,**

$$\underset{KMnO_4}{N_1V_1} = \underset{\text{oxalate soln.}}{N_2V_2}$$

$$\frac{1}{20} \times x = N_2 \times 20$$

$\therefore$ Normality of oxalate solution, $N_2 = \frac{x}{400}$

$\frac{x}{400}$ is the total normality due to oxalic acid and sodium oxalate.

Suppose, strength of oxalic acid = $a$ g/litre

$\therefore$ Strength of sodium oxalate = $(4 - a)$ g/litre

Normality due to oxalic acid, $N_{\text{oxalic acid}} = \frac{a}{\text{Eq. mass of oxalic acid}} = \frac{a}{63}$

Normality due to sod. oxalate, $N_{\text{sod. oxalate}} = \frac{4-a}{\text{Eq. mass of sod. oxalate}} = \frac{4-a}{67}$

$\therefore$ Total normality of the oxalate solution = $N_{\text{oxalic acid}} + N_{\text{sod. oxalate}}$

$$\frac{x}{400} = \frac{a}{63} + \frac{4-a}{67}$$

From this equation, '$a$' can be calculated. Knowing '$a$', the percentage composition of the mixture can be calculated.

% of oxalic acid $= \frac{a}{4} \times 100 = X$ (say)

% of sod. oxalate $= \frac{4-a}{4} \times 100 = Y$ (say).

**Instructions for the Preparation of Solutions**

Provide the following solutions :

1. $KMnO_4$ solution (1.58 g/litre)
2. A mixture of oxalic acid and sodium oxalate
3. 4N $H_2SO_4$.

**Experiment 6: Estimation of Fe(II) and Fe(III) in a given mixture using $K_2Cr_2O_7$ solution.**

**AIM:**

To estimate the amount of ferrous and ferric ions in a given mixture by making use potassiumdichromate

**Chemicals:**potassiumdichromate,Stannouschloride,Mercurouschloride, phenylamine

**Preparationofsolutions**:

**Standardpotassiumdichromate**:

Weigh out accurately weighted 0.245 gm potassium dichromate in to a 100 ml standard flask,dissolveinlittleamountofwaterandmakeupthesolutionwithdistilledwater.Shaketheflaskwellforuniformconcentration.

**Stannouschloridesolution**:

Dissolve150 gmsof$SnCl_2.2H_2O$in100ml concentrated HCl and dilutewith waterto1 litre

**Mecuricchloridesolution**:

Dissolve60 gmsof$HgCl_2$inhotwateranddilute to 1 litre

**Acidmixture**:

Dissolve150 ml ofconcentrated$H_2SO_4$and 50mlof$H_3PO_4$ina reagent bottleand stopperit.

**Phenyl amine:**

Dissolve1 gm ofdi Phenylaminein100ml ofconcentrated $H_2SO_4$

**Procedure:**

**Standardisationoftotaliron:**

Makeupthegivenmixtureof$Fe^{+2}$and$Fe^{+3}$givenin100mlstandardflaskuptothemarkwithdistilled water and shake the flask well for uniform concentration. Pippette out 20 ml of theironsolutionintoaconicalflask,Add100mlconcentratedHClandheatthesolutiontobolingtill the colour of the solution changes yellow. Add stannous chloride drop by drop to the hotsolutiontilltheyellowcolourdisappears.Coolthesolutionundertapandadd100mlmercuricchlorideinoneportionsilkywhitepptofmercurousisobtained.Add5mlofacidmixtureand3-4dropsofdiphenylamineindicator.Titratethesolutionagainststandardpotassium dichromatetakeninaburettetillthegreencolourchangestoblueviolet.Repeatthetitrationtogetconcurrentvalues.Letthetitrevaluebe xml

**Standardisationofferrousiron**:

Pippetteout20mlofthetotalironsolutionintoa250mlconicalflask,

add5mlofacidmixtureand2dropsofof diPhenylamineindicator. Titretheresultingsolutionwithpotassiumdichromate taken in a burette till blue color is obtained. Note the burette readings and repeatthe titrationforconcurrentvalues.Letthe titervaluebe yml

**CALCULATIONS:**

Normality of potassium dichromate $N_1$= Weight of potassium dichromate

×10/49Normalityoftotaliron=$V_1N_1=V_2N_2$

$V_1$= Volume ofdichromate

$V_2$ = Volume of dichromate consumed for total iron$N_2$=Normalityoftotaliron

$N_1$=Normalityofdichromate

$N_2$ = $V_1N_1$/ $V_2$= titre value be x ml × $N_1$/20Amount oftotaliron= $N_2$×55.85= pgms/100ml

10

Normality of ferrous iron $Fe^{+2}$= $V_1N_1=V_3N_3$$V_1$=Volumeofdichromate

$N_1$=NormalityofdichromateV3 = Volume of $Fe^{+2}$ solution$N_3$=Normalityof$Fe^{+2}$solution

$N_3$ =$\underline{V_1N_1}$=titre value be y ml ×$N_1$/20V 3

AmountofFerrousiron =$\underline{N_3\times 55.85}$=q gms/100ml

10

**RESULT:**

Amountof Ferrousiron=Amountoftotaliron-amountof$Fe^{+2}$=p─qgms

100

Experiment 7: Estimation of Fe(III) and Mn(II) in a mixture using standardized$KMnO_4$solution. (Use practical book)

Experiment8:EstimationofFe(III)andCu(II)inamixtureusing $K_2Cr_2O_7$. (Use practical book)

**Paper Code: CEMSEC02P**

# i) Extraction of eucalyptus leaf ingredient

## 1. Introduction:

Eucalyptus comes from the Myrtaceae family, widely grown in the world and commonly used for medicinal plants. There are many species in the world, one of them is Eucalyptus globulus. The essential oil can be found in Eucalyptus globulus, especially in the leaves. The essential oil is used in many sectors, such as health, flavoring, perfume, cosmetics, and pharmaceuticals. The bioactive content in essential oil can be used for antioxidant, anti-bacterial, and anti-inflammatory. In the food sector, the function of essential oil is an additional ingredient for aroma and flavor, and a natural preservative. Eucalyptus leaves have secondary metabolites, such as 1,8-cineole (eucalyptol), monoterpene, sesquiterpene, aldehyde, and ketone. The standard of cineole content in the essential oil must less than 70%. The chemical content in the essential oil depends on the species, geographic location, season, leafage, harvest time, and extraction method. The extraction method can affect the yield and chemical content of the essential oil. The selection of effective extraction methods can produce high quality, maximum yield, and maintain the chemical content. Generally, the extraction methods used are maceration, Ultrasound-Assisted Extraction (UAE), Microwave Assisted Extraction (MAE), distillation with water or steam, and others. The effective extraction method can extract essential oil with the best quality and not damage the existence of bioactive compounds. The review aims to inform the extraction methods of essential oil in Eucalyptus globulus.

## 2. Extraction methods

The extraction method of essential oil can be divided into two categories, conventional and modern methods. The conventional method includes hydro-distillation, steam distillation, and extraction using solvents. The modern method includes supercritical fluid extraction, microwave-assisted hydro distillation, and ultrasound-assisted extraction.

### 2.1. Hydro-distillation

This method is a traditional extraction method used for essential oil. In this method, the essential oil is evaporated by heating a mixture of water and material or with other solvents, then the vapor is liquefied in the condenser. The result then flows into a separate room in which there will be separated into essential oil and water. This method is quite simple, it can be used in either a small or big scale, can avoid chemical content loss due to the long extraction process, and saves energy used. In eucalyptus essential oil extraction, 15 grams of sample was immersed in 300 ml water and distilled for 5 hours. The oil extracted by hydro-distillation contained volatile compounds while the oil from SFE and soxhlet contained volatile and higher molecular weight compounds. The Eucalyptus oil yield from 3.1 at 1 h to 3.8% at 5 h of hydro-distillation extraction.

**2.2. Steam distillation**

This method is a standard method used for temperature-sensitive materials (such as oil, resin, hydrocarbon, and many others), insoluble in water, and can decompose at its boiling point. The mechanism of this method is separation compound or a mixture of the compound at the boiling point below the boiling point of the compound (close to the boiling point of water, 100oC at atmospheric pressure) so that the volatile components whose boiling point of 150 to 300 ° C can be evaporated at the water temperature. Water vapor is passed to the material that will be distilled without immersing the material in water. Furthermore, the compounds included in the water vapor enter the condenser and then are separated for its water and essential oil compound. The essential oil that has been cooled and returns to liquid comes down from the condenser and is collected in the container under it, called a separator. In this separator flask, the water and essential oil gather with the position of the essential oil is floating on the water. Eucalyptus globulus' essential oil extraction, generally, uses this method. The part used in the process is a fresh or dry leaf with oil yields 1.0% - 2.4% (fresh weight) using fresh or dry leaf.

**2.3. Solvent extraction**

Solvent extraction, liquid-to-liquid separation, is a separation method based on solubility. Solvent extraction is commonly used in the processing of perfumes, vegetable oils, or biodiesel. Solvent extraction is used for soft texture or fragility plants, sensitive to heat, and large quantities of essential oils with low cost. E. Globulus leaves were cleaned, air-dried for 4 days until the average humidity is around 9%, then ground, sieved to pass 0.5mm, and packed in sealed plastic bags. Eucalyptus leaves were extracted in an orbital shaker with

temperature control using aqueous ethanol as solvent. Two grams of leaf powder then put in 100ml erlenmeyer using a solid/liquid ratio of 1:20 g/mL then a shaking speed of 120 rpm. The extract was filtered using filter paper under vacuum, and the filtrate obtained will be analyzed. The results extraction ranged from 24.4 to 33.1%.

**2.4. Supercritical fluid extraction**

Supercritical Fluid Extraction (SFE) refers to a separation process of a component from the matrix using supercritical fluid as the extraction solvent. The extraction was usually from a solid matrix or liquid. In general, the supercritical fluid used CO2, but it was modified by the addition of other solvents like ethanol or methanol. This extraction method obtained a higher yield, higher diffusion coefficient, lower viscosity, and better extract quality (functional and biological activities) than the conventional method. However, the disadvantage of the SFE method was costly (the price of the equipment), and it was not easy to handle or operate. E. Globulus leaves were air-dried for two days and by drying the samples in the oven set at 103◦C for 5 h. Then, the samples were ground with a knife grinder and the ground sample was sieved using a sieve shaker. Five g of eucalyptus leaves were weighed and put in the SC $CO_2$ extraction vessel. Installing glass wool at both ends of the extractor to prevent the entry of the substrate. SFE can be started when the pressure and temperature are appropriate. The flow rate of gas $CO_2$ was set at 2 L/min in all runs. Results extract included in the amber bottle, the bottle was placed in an ice bath for dynamic extraction step, which can also function in minimizing the loss of volatile compounds due to the sublimation of $CO_2$. Deposition in all the pipes is washed using ethanol and then mixed with the extract collected in a bottle. Then put in a rotary evaporator and conducted weighing the extract. The resulting oil has increased along with the increasing pressure and temperature at 50 ° C of 2.99% to 3.39% and at 70 ° C of 2.51% to 4.66% at 70 ° C. The extraction E.globulus with this method at pressure (350 bar), temperature (80 $^{o}$C) and flow rate of $CO_2$ (12 g min-1) gave the highest percentage yield (3.6%) compare with hydro distillation, solvent extraction, and ultrasonic-assisted extraction method.

**2.5. Microwave-assisted hydro-distillation**

Microwave-Assisted Hydro-distillation is the hydro-distillation technique through a microwave oven during the extraction process. This method successfully reduced the required time and solvent volume of the extraction, minimized the environmental impact by releasing less $CO_2$ in the atmosphere, and required less energy. On the other hand, this method was

also able to foster the purify of essential oil. Extraction of essential oil from E. globulus leaves with this method at the ratio of raw materials to water is 1:3 mL/g, with 60 min in extraction time, and 450W microwave power can give yield 2.65 mg/L (ground material) with the main ingredients of essential oils were Eucalyptol (38.771%).

**2.6. Ultrasound-assisted extraction**

Ultrasound-assisted extraction was defined as the extraction method which producing high-value compounds. This method was beneficial for extracting the essential oils, especially from flowers, leaves, or seeds. Although requires a high price, this method increases yield in a shorter time. The research was done byrevealed that the yield produced by this method on Eucalyptus globulus leaves was higher than the hydro-distillation and extraction method a (2.2%) with important compounds extracted are aliphatic saturated hydrocarbons, organic acids, and esters.

## ii) Extraction of eugenol from clove

**1. Introduction**

Eugenol is a phenolic component that can be obtained from a wide range of plant sources including clove oil, nutmeg oil, cinnamon extract and many other plants. It owns strong health promoting functions that make it a versatile natural ingredient. Eugenol was first extracted from the leaves and buds of Eugenia caryophyllata commonly named as clove. Currently, eugenol can also be synthesized by allylation of guaiacol with allyl chloride having the similar kind of functional property. Eugenol is present in significant amounts in the extracts of numerous medicinal herbs so it has fascinated the attention of several researchers and opened up the gateway of research regarding its utilization as a medicine to cure various diseases. Eugenol is avowed to possess certain pharmacological properties including anesthetic activity, antioxidant potential,antimicrobial role, anti-inflammatory action, anti-carcinogenic effects, neuroprotective ability, hypolipidemic efficiency, and anti-diabetic effectiveness.

**2. Extraction methods**

**2.1 Steam distillation**

The most common method for the isolation of eugenol is steam distillation. In the extraction and isolation process of eugenol, firstly essential oil is extracted from the plants. Afterwards, the essential oils are mixed with 3% solution of sodium or potassium hydroxide for the extraction of eugenol. This reaction results in the formation of a phenolic alkali salt. The insoluble portion of the extract is then isolated by solvent extraction or steam distillation. The remaining alkaline solution is then acidified at refrigeration temperature followed by the liberation of eugenol by employing various techniques such as fractional distillation, high-pressure liquid chromatography (HPLC) or thin-layer chromatography (TLC). At the end, the purity of the obtained eugenol is verified by employing modern spectroscopic techniques like Fourier transform infrared spectroscopy (FTIR), Fourier transforms near infrared spectroscopy (FTNIR), mass spectroscopy (MS) and nuclear magnetic resonance (NMR). Some important methods for the extraction of eugenol from various plant sources are described herein.

**2.2 Solvent extraction**

Solvent extraction is one of the most common and extensively employed methods for the extraction of essential oils from plants. Accordingly, eugenol has also been extracted using various solvents like methanol, ethanol, petroleum ether and N hexane. The major hindrances of solvent extraction are inclusion of other soluble residues undesirable flavor changes in the food. However, still this method has wide applications for the extraction of eugenol and other essential oils from various aromatic herbs. In a typical solvent extraction process of eugenol from clove, the clove buds are ground and wrapped in filter paper followed by subjecting the filter paper to the extraction thimble and inserting into the reflux flask having 500 mL capacity. Afterwards, extraction is carried out by using a suitable organic solvent in Soxhlet apparatus. The process ends by concentrating the obtained extracts at 50 °C using rotary vacuum evaporator.

**2.3 Hydro distillation**

Hydro-distillation is also one of the mostly used methods for the extraction of essential oils.9 During hydro distillation method, powdered sample (100 g dried and ground clove buds) is soaked into water. To carry out hydro-distillation, dried clove sample is taken into 500 mL volumetric flask and subjected to hydro-distillation for 4–6 hours. Subsequently, the volatile distillate is collected and saturated with sodium chloride following the addition of petroleum ether or other suitable organic solvent. Later, hydro and ether layers are separated and

dehydrated by using anhydrous sodium sulphate. Eventually, the sample is heated in water bath at 60 °C for the recovery of ether and concentration of extract. The average yield of oil using hydro-distillation is about 11.5% whereas reported eugenol concentration is 50.5–53.5%. However, extraction yield can be increased by reducing the particle size of ground clove buds.

## iii) Extraction of nicotine from tobacco

### 1. Introduction

Tobacco (Nicotiana tabacum L.) belongs to the genus Nicotiana and is native to America. This plant is farmed over the northern and northeastern area in Thailand and has utility primarily for the raw material for making cigarettes under the Tobacco Authority of Thailand (TOAT) organization. Unlike most crops, it is the leaves of the tobacco plant that are of economic importance. Beginning at the bottom of the plant, tobacco leaves are generally classified into four main groups: lug, cutter, leaf, and tip. The lowermost four or five leaves, which are referred to as lugs, have the lowest nicotine concentration, have the highest reducing sugar concentration, and contain the least amount of aroma and flavor relative to the middle (cutter) and upper-stalk (leaf and tip) positions. Burley tobacco, which is an important economic tobacco variety in Thailand, is marketed on a grade basis, and the position of the leaves on the stalk is closely related to the grade. Therefore, the chemical compositionoftheleavesasrelatedtopositiononthestalkshouldsupplyvaluable information regarding their suitability for a particular use. Nicotine (NCT) is an alkaloid contained in tobacco leaves. NCT is soluble in some types of solvents, such as alcohol,chloroform, ether, petroleum ether, kerosene, and water. Therefore, various solvents can be used to isolate nicotine from tobacco leaves by using a solvent extraction method.

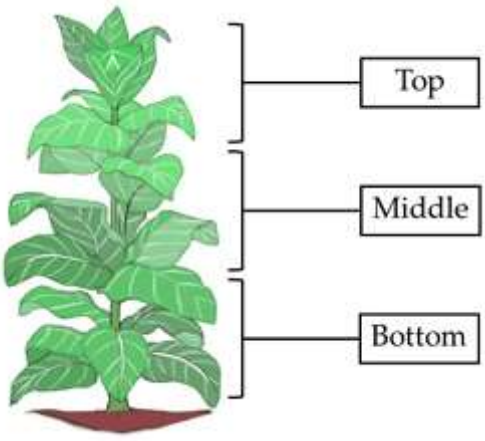


Figure 1. Burley tobacco plant variety showing approximate stalk position of farmers' grades

**2. Extraction method**

The three parts of N. tabaccum leaves—top, middle, and bottom—were dried in an oven at 55°C. The dry N.tabaccumleaves were extracted by 3 methods: water maceration extraction, ethanol maceration extraction, and acid-base extraction.

**2.1. Maceration extraction**

**For maceration extraction**, 50 g of tobacco leaves were macerated (48 h 3 times) at room temperature (25°C) in 750 mL of each solvent. The extracts from the 3 macerations were pooled, filtered and subjected to a rotary evaporation to obtain crude extracts.

**2.2 Acid-base extraction**

Acid-baseextractionis based on the alkaloid property of nicotine, which involves different solubility levels in water and an organic solvent. The 50 g of tobacco leaves was boiled with 750 mL of water at 80 °Cfor20min, then 10 gofsodium carbonate was added and the mixture was continuously heated for 10 min. After filtration, the obtained filtrate was adjusted to pH 12 using sodium hydroxide and extracted with chloroform (100 mL 2 times) using the liquid-liquid extraction technique. The chloroform of the filtrate was removed using a rotary evaporator at 50 C under vacuum to obtain crude extracts.

Each extraction method was performed in duplicate. The obtained crude extracts were stored at 4 °C and protected from light until further study. The calculation of tobacco leaf extract yield is shown in Equation (1), as follows:

Yield of tobacco leaves extract = (Weight of extract/Dry weight of tobacco leaves)*100%....(1)

## iv) Curumine from turmeric

**1. Introduction**

Curcumin, also known as diferuloymethane, is a hydrophobic polyphenol derived from the rhizome of perennial herbs genus Curcuma which belongs to the ginger family

(Zingiberaceae) and includes species like Curcuma longa, Curcuma amada, Curcuma zedoaria, Curcuma aromatic, Curcuma raktakanta. Among these species, Curcuma longa (turmeric) is the most popular. Generally, turmeric rhizomes contain 3-5% of three types of curcuminoid derivatives including curcumin (75%), demethoxycurcumin (10-20%) and bisdemethoxycurcumin (5%), curcumin being the most important bioactive compound. Curcumin has long been used as a spice and a natural coloring agent in Indian curries, as well as a component of Chinese traditional medicines. As a food additive, its E number (codes for substances used as food additives for use within the European Union (EU) and European Free Trade Association (EFTA)) is E100. In recent years, numerous in vivo and in vitro studies have revealed that curcumin has various physiologic activities, and worldwide attention has therefore been focused on curcumin. Curcumin has been found to have multiple actions such as anti-oxidant through scavenging of free radicals, anti-inflammatory by suppression of NF-kB and AP-1 activation, anti-cancer through inhibition of cancer cell proliferation, induction of apoptosis, suppression of angiogenesis, inhibition of the expression of anti-apoptotic proteins, protection of the immune system, and anti-bacterial/fungal/viral activities. Due to its wide range of pharmacological activities, curcumin shows potential for commercial use in different industries including food, cosmetics and pharmaceutics.

**2. Extraction method**

**2.1 solid-liquid extraction**

Solvent extraction of solid samples, which is commonly known as “solid-liquid extraction”, (also referred to as “maceration” or “soaking”), is a well-understood and widely-used method. It was found that extraction with ethanol gave the highest yield (0.26 mg/10 g) when the extraction was performed at 30°C for 1 h with a solid to solvent ratio of 1:8. Consistent with this, ethanol was the most preferred solvent for extraction of curcumin among all organic solvents employed. Moreover, the ethanol concentration of the solvent mixture plays a crucial role in determining the extraction efficiency.

**2.2 Ultrasound-assisted extraction (UAE)**

Ultrasound works on the principle of tandem compression and expansion induced by sound waves with the frequency range of 20 kHz-100 MHz. The ultrasonic waves induce micro bubbles formation, and the breakage of these bubble lead to cavitation phenomenon, which

results in intense shear forces, shock waves, macro-turbulences, micromixing and acoustic streaming.

## v) Extraction of caffeine from tea/coffee

### 1. Introduction

Caffeine is a naturally occurring alkaloid produced by tea and coffee shrubs. It is a CNS stimulant that is believed to act by serving as an antagonist of adenosine receptors on neurons.Caffeine is soluble in hot water and is extracted from coffee grounds or tea leaves when these products are brewed. While caffeine is water soluble, it is much more soluble in the organic solvent methylene chloride ($CH_2Cl_2$). Methylene chloride is immiscible with water and when mixed separates from water to form a two-layer mixture. Because methylene chloride is denser than water it usually comprises the lower layer in the two-part mixture. By mixing brewed tea with methylene chloride, the caffeine can be extracted into the organic layer. Since the organic layer is immiscible with water, it can be removed after it separates from the water, and the solvent evaporated to give nearly pure caffeine.

### 2. Extraction method

#### 2.1 Extraction of the Caffeine from the Tea

When the tea has cooled to room temperature, add 3 mL of methylene chloride ($CH_2Cl_2$) to each centrifuge tube. Cap the tubes and gently shake for several seconds, carefully vent the tubes to release any pressure buildup by slowly opening the caps. Recap the tubes and shake for about 30 seconds (vent the tube occasionally). An emulsion will likely form during the extraction process. To “break” the emulsion, spin the tubes in the centrifuge for 2-3 minutes. Make sure the centrifuge is balanced with tubes of nearly equal mass opposite of each other in the rotor. The mixture should have two layers—a nearly colorless bottom layer and a dark upper layer. If a third frothy green-brown layer is in between the upper and lower layers, the emulsion is still present and the tubes should be centrifuged again.

#### 2.2 Transferring and Drying the Methylene Chloride Solution

Using the plastic pipette, remove the lower organic layer and transfer it to a 25 mL Erlenmeyer flask, try not to transfer any of the dark aqueous layer. Add a fresh 3 mL portion of methylene chloride to each tube, cap and shake for about 30 seconds to extract the tea again. Be sure to occasionally vent the centrifuge tube. Centrifuge the tubes again as

described above. Remove the bottom organic layer and combine with the first extracts in the 25 mL Erlenmeyer flask. Again, try not to transfer any of the dark aqueous layer. Add anhydrous sodium sulfate (Na2SO4) to the combined methylene chloride extracts to remove any traces of water. Add small spatula tips full of the sodium sulfate until the crystals no longer clump. Allow this mixture to stand for 10 minutes.

**2.3 Evaporating the Solvent and Recording Mass of Caffeine**

Weigh a second, dry 25 mL Erlenmeyer flask and record the mass on your data sheet. Transfer the dried methylene chloride extracts to the flask using a dry pipette. Be careful not to transfer any of the solids. Place the flask on the steam bath in the fume hood to evaporate the methylene chloride. Remove the flask from the steam bath as soon as all the solvent has evaporated, otherwise you may lose some of the caffeine by sublimation. Dry the outside of the flask with a paper towel, weigh the flask with contents, and record the mass on your data paper.

**2.4 Measuring the Melting Point of the Recovered Caffeine**

Scrape as much of the caffeine from the flask as possible using a spatula. Load a capillary tube with about 2 mm of the caffeine and determine the melting point using the Melting point apparatus.

## Paper Code: CEMMI02P

**Organic Chemistry Lab**

**Qualitative Analysis of Single Solid Organic Compound(s)**

**Background**

Organic chemists often must identify unknown compounds. In some cases, such as a reaction, you may have a good idea of what the compound in question is. However in other cases, such as when you isolate a compound from a natural source, you may have no idea what the compound might be. In this experiment you will determine the identity of an unknown compound. First,you will need to purify your compound, then you will need to identify its functional group (it will contain only one), and finally you will need to make a derivative of the compound. You will confirm your results with boiling or melting point, IR, and NMR.

Impurities in your compound will make it extremely difficult to identify. Thus, before you do anything else, you will need to make sure your unknown compound is pure. Consider each of the following purification techniques you have learned over the courseof the year.

1. *Recrystallization:* Works well for solid compounds. You will need to find an appropriate recrystallization solvent. Consider a variety of solvents and mixed solvent systems.
2. *Distillation:* Works well for liquids that have a boiling point of <250 °C. (Note: Fractional distillation may be required if you suspect impurities close to the boiling point of your unknown.)
3. *Column Chromatography:* Works well for UV active compounds. You will need to use TLC to identify a solvent system that will separate your unknown from any impurities.

After you have purified your unknown, verify that it is pure enough to proceed by measuring the boiling or melting point. Note that while you will not know what the melting point or boiling point of your unknown should be, the narrowness is an excellent indicator of whether or not your product is pure. Also pay attention to the appearance of your unknown and see if it has changed (hopefully for the better) during the course of the purification process.

Once your unknown is pure, you will need to identify its functional group. Your unknown will have one major functional group (alcohol, ketone, aldehyde, amide, amine, carboxylic acid, or ester). Additionally, your unknown compound may or may not contain an aromatic ring. To determine the functional group, it is recomanded that you start with solubility tests, and then conduct functional group classification tests. IR spectroscopy may also be useful at this point.

Solubility can sometimes provide a surprisingly useful amount of information. First, you will test your unknown's solubility in water. Compounds with 4 carbons or less will easily dissolve in water, whereas compounds with 8 carbons or more will be insoluble. Compounds containing 5----7 carbons may or may not dissolve (often they will display "partial" solubility). If your compound dissolves in water, you will also want to check the pH of the solution. Amines will typically be basic, and carboxylic acids will typically be acidic. Most other compounds will be neutral. Compounds that are insoluble in water should then be subjected to a solubility test in 5% HCl. Typically, only amines will be soluble in HCl because they form water-soluble hydrochloride salts when they react with HCl. Compounds that are not soluble in HCl, should be subjected to testing in basic solutions (5% NaOH and 5% NaHCO3). Both strong and weak acids (Carboxylic acids and phenols) will be deprotonated by NaOH to form water-soluble alkoxides. Only strong acids like carboxylic acids will react with NaHCO3. Compounds that are not soluble in base should then be reacted with a very strong acid, sulfuric acid (note that in the case of sulfuric acid, "solubility" is also indicated by any type of reaction such as heat, gas generation, or a color

change). Compounds that cannot become protonated by sulfuric acid at all (i.e., alkanes, alkyl halides, and aromatic carbons) will still remain insoluble.

The results from the solubility tests can significantly help in determining which classification tests should then be performed, or at least narrow down the list. By no means do you need to conduct all classification tests. In fact, you should do your best to select only tests that will provide you with additional information about your unknown and/or confirm results. Also, make sure that your glassware is clean and dry so you do not get any false positive or false negative results. Keep in mind that a negative result for a classification test provides useful information, so be sure to keep track of negative results as well as positive results. Also, for each classification test that you perform, be sure to run a blank, and one or more controls. These will help you to determine if a reaction actually occurred. A blank includes everything but the unknown, and a control includes a compound for which the outcome is known in place of the unknown. Controls can be positive (a compound you know will react) or negative (a compound that you know will not react). The classification tests are summarized in the table below.

| Functional group | Test | Test no | Notes |
|---|---|---|---|
| Elemental analysis | Lassaigne test | C-1 | Test for nitrogen, sulphur, halogens |
| Amine | Basicity test<br>Bleaching powder test<br>Dye test | C-2<br>C-3<br>C-4 | Test for aromatic amine |
| Nitro | Reduction test<br>Muliken and barker test | C-5<br>C-6 | Test for aromatic nitro group |
| Amido | Nitrous acid test<br>Hydrolysis test | C-7<br>C-8 | Test for amido group |
| Phenolic –OH | Ferric chloride test<br>Back dye test | C-9<br>C-10 | Test for phenolic-OH |
| Carboxylic acid | Bicarbonate test<br>Esterification test | C-11<br>C-12 | Test for carboxylic acid |

| | | | |
|---|---|---|---|
| Aldehyde | Benedict test<br>Tollens test | C-13<br>C-14 | Test for aldehyde |
| Ketone | 2,4-Dinitrophenoyl Hydrazine test | C -15 | Test for ketone |

At this point, you should be able to use your boiling or melting point data combined with the results of your functional group data to develop a hypothesis as to what your unknown might be or at least narrow down the list to only a few candidates. Note tha due to the accuracy (or lack thereof) of our thermometers, your boiling or melting points may be up to 15°C lower than the literature values.

Once your functional group has been determined, you will prepare a derivative of your unknown. To prepare a derivative, you will select a suitable reaction that converts your unknown into a different functional group for which the boiling or melting point is known. This is particularly useful because compounds that have similar boiling or melting points will oftenhave derivatives that differ significantly in terms of boiling or melting point. You should then be able to identify your unknown using this information.

Finally, you can confirm the identity of your product using IR and NMR. Note that these measurements can be taken at any time during the course of the lab after you purified your product. In fact, it is recommended that you conduct them sooner rather than later as they may provide valuable information as to the identity of your unknown (e.g., IR may reveal your functional group).

**Lab Notebook Preparation A**

Before coming to lab on the first day of this experiment, the following items must be in your lab notebook:

1. Title of experiment
2. Date the experiment is to be performed
3. Outline of your plan for determining the identity of your unknown

4. Hazards of and appropriate precautions for the safe handling of unknown organic compounds
5. References

**Lab Notebook Preparation B**

Before coming to lab on the day you plan to prepare a derivative, the following items must be in your lab notebook:

1. Title of experiment
2. Date the experiment is to be performed
3. List of possible unknowns
4. The chemical reaction(s) you are attempting (with skeletal structures…R groups are okay if you do not know the identity of your unknown yet)
5. For each reaction you are attempting, include a table with information about your starting materials. Include molecular weight, molar equivalents, and mmoles to be used. For solids include grams. For liquids, include grams, density, and volume. For solutions, include the concentration and volume. (Note: You will not be able to completely fill in the table if you do not know the identity of your unknown yet. If that is the case, list whatever data you can.)
6. Any relevant physical properties (i.e., melting points or boilingpoints of possible unknowns and their derivatives)
7. Hazards of and appropriate precautions for the specific reaction(s) you are conducting
8. References

**Safety Notes**

- Assume that all unknowns are flammable and harmful by inhalation, ingestion, and skin absorption. Do not inhale their vapors and avoid contact with eyes, skin and clothing.

**Directions**

1. Purify your unknown using distillation, recrystallization, or column chromatography. It is recommended that purify the entire unknown provided so that you have enough pure material for all of the tests.

2. Measure the boiling or melting point of your unknown to confirm its purity.

3. Confirm with your instructor that the boiling or melting point you obtained for your unknown is within 15 °C of the reported literature value before proceeding.
4. Test the solubility of your unknown in water. (If your unknown is a solid, crush it into a fine powder.)

    a. Add approximately 30 mg of your unknown to a test tube or smallvial.

    b. Add 1 mL of water and shake vigorously for approximately 30 seconds. If the unknown appears to be soluble, test the pH of the solution and then skip to step 9.

5. Test the solubility of your unknown in 5% HCl. (If your unknown is a solid, crush it intoa fine powder.)
    a. Add approximately 30 mg of your unknown to a test tube or small vial.

    b. Add 1 mL of 5% HCl and shake vigorously for approximately 30 seconds. If the unknown appears to be soluble, skip to step 9.

6. Test the solubility of your unknown in 5% NaOH. (If your unknown is a solid, crush it into a fine powder.)

    a. Add approximately 30 mg of your unknown to a test tube or small vial.

    b. Add 1 mL of 5% NaOH and shake vigorously for approximately 30 seconds. If the unknown appears to be insoluble, skip to step8.
7. Test the solubility of your unknown in 5% NaHCO3. (If your unknown is a solid, crush it into a fine powder.)

    a. Add approximately 30 mg of your unknown to a test tube or small vial.

    b. Add 1 mL of 5% NaHCO3 and shake vigorously for approximately 30 seconds.

8. Note whether your unknown is soluble or insoluble and then skip to step 9.

9. Test the solubility of your unknown in concentrated H2SO4. (If your unknown is a solid,

    crush it into a fine powder.)

a. Add approximately 30 mg of your unknown to a test tube or small vial.

b. Add 1 mL of concentrated $H_2SO_4$ and shake vigorously for approximately 30 seconds.

c. Note whether your unknown is soluble or insoluble. (Any indication of a reaction such as heat, gas generation, or a color change also indicates solubility.)

10. Conduct classification tests as needed. See directions for specific tests below.

11. Confirm the identity of your functional group with your instructor before proceeding.

12. Prepare one or more derivatives of your unknown. See directions for specific derivatives below.

13. Measure the melting point of any derivatives.

14. Confirm with your instructor that the melting point you obtained for your derivative is within 15 °C of the reported literature value.

**Classification Tests**

***C-1 Elemental Analysis***

This reaction tests for the presence of nitrogens, sulphur and halogens.

*Safety Notes:* Sodium can cause serious burns and the sodium-lead alloy may react violently with some substances. Wear gloves, avoid contact, and keep the sodium-lead alloy away from other chemicals.

*Recommended Controls:* butylamine, acetamide, bromobenzene

*Procedure:*

1. In the fume hood or under a snorkel, place 0.25 g of 10% sodium-lead alloy in a small, dry test tube held vertically by a clamp.

2. Melt the alloy with a Bunsen burner flame and continue heating until the sodium vapor rises about 1 cm up the tube.

3. Using a Pasteur pipet, add 2 drops of the unknown (or 10 mg of a solid) directly onto the molten alloy so that it does not touch the sides of the tube.
4. Heat gently to start the reaction, remove the flame until the reaction subsides, then heat the tube strongly for a minute or two, keeping the bottom a dull red color.
5. Let the tube cool to room temperature.
6. Dropwise add 1.5 mL of water and heat gently for a minute or so until the excess sodium has decomposed and gas evolution ceases.
7. Filter the solution through a Pasteur pipet with a small plug of cotton, wash the cotton with 1 mL of water, and combine the wash water with the filtrate. (Use a rubber bulb to expel any liquid that adheres to the cotton.) The filtrate should be colorless or just slightly yellow. If it is darker, repeat the fusion with stronger heating or more of the alloy.

*To test for nitrogen:*

1. Put 5 drops of the sodium fusion solution into a small test tube.
2. While stirring, add enough solid sodium bicarbonate, to saturate it (a little excess solid should be present).
3. Add 1 drop of this solution to a test tube containing 10 drops of PNB reagent (*p*-nitrobenzaldehyde in dimethyl sulfoxide) and note any color change.

*To test for halogens:*

1. Acidify 10 drops of the sodium fusion solution with dilute nitric acid.
2. Boil it gently under the hood for a few minutes.
3. Add a drop or two of 0.3 M aqueous silver nitrate, and note the color and volume of any precipitate that forms. (If a voluminous precipitate forms, let the precipitate settle and then remove the solvent using a pipet.)
4. Add 2 mL of 3 M aqueous ammonia to the solid, shake vigorously, and note your observations.
5. To test further for bromine and iodine, acidify 1 mL of the original sodium fusion solution with 1 M sulfuric acid, boil for a few minutes, and add 0.5 mL of dichloromethane and a then a drop of freshly prepared chlorine water. Shake and look for a color in the dichloromethane layer.

To test for sulphur:

1. Put 1ml of sodium-extract into a test tube.
2. Add 1 ml dil.NaOH solution followed by 2-3 drops of sodium nitroprusside.

***Interpretation****:* In the PNB test, a purple color indicates the presence of nitrogen (green indicates sulfur). In the halogen tests, formation of a voluminous precipitate on addition of silver nitrate indicates that a halogen is present, and the color of the precipitate (a silver halide) may suggest which halogen: white for chlorine, pale yellow for bromine, and yellow for iodine. If only a faint turbidity is produced, it may be caused by traces of impurities or by incomplete sodium fusion. If the precipitate is silver chloride, it will dissolve in aqueous ammonia; silver bromide is only slightly soluble and silver iodide is insoluble. In the chlorine water test, a red-brown color is produced by elemental bromine and a violet color by elemental iodine. In the sulphur test, a violet or purple color indicates the presence of sulphur.

***C-2 Basicity Test***

This test is useful if you have already determined that you have an amine. It is used to distinguish alkyl amines from aromatic amines.

*Recommended Controls: p*-toluidine, dibutylamine

*Procedure for water-soluble compounds:*

1. Dissolve 4 drops of your unknown (0.10 g of a solid) in 3 mL of water.
2. Measure the pH of the solution using pH paper.

*Procedure for water-insoluble compounds:*

1. Dissolve 4 drops of your unknown (0.10 g of a solid) in 3 mL of a pH 5.5 acetate-acetic acid buffer.
2. Mix thoroughly.

*Interpretation:* Water-soluble alkyl amines give pH values above 11, whereas water-soluble aromatic amines have pH values below 10. Water-insoluble alkyl amines should dissolve in the buffer, but water-insoluble aromatic amines will not dissolve.

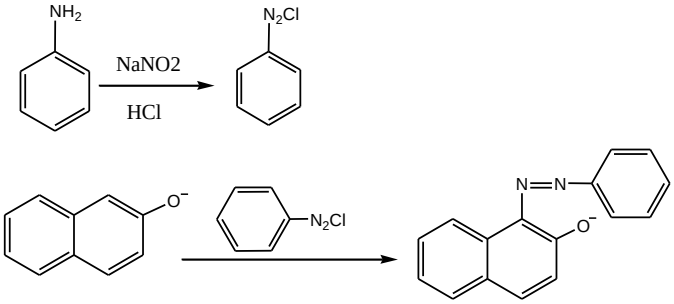
***C-3 Bleaching powder test***

*Procedure:*

1. Dissolve 0.05 g of your unknown in 5 mL of water.
2. Add 3-4 drops of bleaching powder solution.
3. Shake vigorously.

*Interpretation: Transient purple color which soon turns brown or light purple color.*

***C-4 Dye test:***

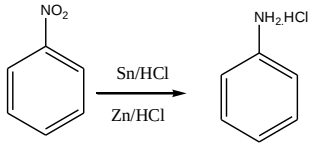



Procedure:

1. 0.1 g of organic sample is dissolved in 5ml of dil.HCl.
2. The mixture is cooled at 0º-5ºC in an ice-bath.
3. Then add 1ml of ice cold solution of dil. $NaNO_2$.
4. The mixture is added to ice-cold alkaline solution of β-Napthol.

*Interpretation:* Red or orange red dye (brown or raddish purple or violet dye indicates the presence of two amino groups; soluble dye indicates the presence of SO3H or Ar-OH along with Ar-$NH_2$ group).

***C-5 Reduction test***




1. A mixture of 0.1 g of organic sample, few pieces of granulated tin or zinc and 3ml of Conc. HCl is warmed gently with occasional shaking till the reaction is complete.
2. The mixture is cooled.
3. Filtered, if required, diluted and diazo-coupling reaction is performed.

*Interpretation:* Brilliant red or scarlet dye obtained.

***C-6 Muliken and Barker Test***

Procedure:

1. 0.1 g of organic sample is dissolved in 5 ml of 50% alcohol.
2. A little solid $NH_4Cl$ or 10% $CaCl_2$ solution and a pinch of Zn-dust is added to it.
3. The mixture is boiled for a few minutes.
4. Then the mixture is cooled and allowed to stand for 5 minutes and then filtered.
5. With the filtrate following three tests are performed:

a) A portion of the solution is added to Tollen's reagent and then warmed in a water bath.

b) Two drops of benzoyl chloride and 2 drops of conc. HCl are added to another portion of the filtrate followed by 12 drops of $FeCl_3$ solution.

c) The last portion of the filtrate is warmed with a little Fehling's solution.

*Interpretation:* From the part (a), a silver mirror or black or grey precipitation is obtained. From part (b), a wine-red color of ferric hydroxamate is present, from last part (c), a red precipitation is obtained.

***C-7 Nitrous Acid Test***

Procedure:

1. A little of the aqueous solution of organic sample is treated with with a few drops of $HNO_2$ (NaNO2 and HCl).

*Interpretation:* Effervescence due to evolution of $N_2$ gas.

***C-8 Hydrolysis Test***

Procedure:

0.2 g of organic sample is heated with 2ml of 50% NaOH solution.

*Interpretation:* Characteristics smell of $NH_3$ which turns mercurous nitrate paper black or copper sulphate paper deep blue.

***C-9 Ferric Chloride***

This reaction tests for the presence of phenols.

*Recommended Control:* phenol

*Procedure:*

1. Dissolve 1 drop of the unknown (40 mg of a solid) in 1 mL of water. If( you know based on the results of your solubility tests that the unknown is insoluble in water, use 0.5 mL of water and 0.5 mL of methanol instead of 1 mL of water.)
2. Add two drops of 2.5% ferric chloride solution.

*Interpretation:* Formation of an intense red, green, blue, or purple color suggests a phenol or an easily enolizable compound (such as an aldehyde or ketone). Some phenols do not react under these conditions.

***C-10 Back Dye Test***

This reaction tests for the presence of phenols.

*Procedure:*

1. A few drops of aniline dissolved in dil. HCl.
2. Few drops of cold dil. $NaNO_2$ solution is added.
3. Then the clear solution is added to the cold solution of organic sample in NaOH.

*Interpretation:* A brilliant red dye is obtained. Phenolic OH group present and confirmed.

***C-11 Bicarbonate Test***

This reaction tests for the presence of carboxylic acid.

*Procedure:*

1. A small amount of organic sample is sprinkled over aqueous solution of sodium bicarbonate.

*Interpretation:* Effervescence due to the evolution of $CO_2$.

***C-12 Esterification Test***

This reaction tests for the presence of carboxylic acid.

1. 0.5 g of organic sample is taken in a dry test tube.
2. To this, add 1 ml of dehydrated ethanol.
3. Then 2-3 drops of conc. $H_2SO_4$ is added and heated for 5 minutes in a water bath.
4. The mixture is then poured into a beaker containing large volume of $Na_2CO_3$ solution.

*Interpretation:* Characteristics sweet fruity smell of ester.

***C-13 Benedict's Test***

This reaction tests for the presence of aldehydes. Note that most ketones and aromatic aldehydes will not react.

*Recommended Controls:* butanal

*Procedure:*

1. Add 2 drops of the unknown (80 mg if it is a solid) to 2 mL of water.

2. Add 2 mL of Benedict's reagent.
3. Heat the mixture to a boil.
4. Observe if a precipitate forms, and note its color.

*Interpretation:* Benedict's reagent contains copper(II) sulfate,sodium citrate, and sodium carbonate. Aldehydes will react with the Cu2+ from the copper(II) sulfate to form copper(I) oxide which appears as a yellow or orange precipitate (it may look a little green in the blue reaction solution). Note that most ketones and aromatic aldehydes will not react.

***C-14 Tollen's Test***

This reaction tests for the presence of aldehydes.

*Recommended Controls:* benzaldehyde

*Procedure:*

1. Measure 2 mL of 0.3 M aqueous silver nitrate into a test tube and add 1 drop of 3 M sodium hydroxide.
2. Add 2 M aqueous ammonia drop by drop, with shaking, until the precipitate of silver oxide just dissolves (avoid an excess of ammonia).
3. Add 1 drop of the unknown (40 mg of a solid) to this solution, shake the mixture, and let it stand for 10 minutes. (If a silver mirror is observed at this point, this is considered a positive result.)
4. Heat the mixture in a 35 °C water bath for 5 minutes.
5. Immediately after the test has been completed, dissolve any solid residue in 1M nitric acid and then dispose of the solution in the designated waste container.

6. *Interpretation:* Formation of a silver mirror on the inside of the test tube is a positive test for an aldehyde. (Note that if the tube is not sufficiently clean, a black precipitate or a suspension of metallic silver may form instead.)

***C-15 2,4-Dinitrophenylhydrazine***

This reaction tests for the presence of aldehydes and ketones.

*Safety Notes:* 2,4-Dinitrophenylhydrazine (DNPH) is harmful if absorbed through the skin. Wear gloves and avoid contact.

*Recommended Controls:* cyclohexanone, benzaldehyde

*Procedure:*

1. Dissolve 1 drop of the unknown (40 mg of a solid) in 1 mL of 95% ethanol (use more ethanol if necessary to completely dissolve the unknown).
2. Add this solution to 2 mL of the DNPH reagent.
3. Shake and let the mixture stand for 15 minutes or until a precipitate forms. (If a precipitate is observed at this point, this is considered a positive result.)
4. Scratch the inside of the test tube and observe if a precipitate forms, and note its color.

*Interpretation:* Formation of a crystalline yellow or orange-red precipitate indicates an aldehyde or ketone. The color of the precipitate may give a clue to the structure of the carbonyl compound (unconjugated aliphatic aldehydes and ketones usually yield a yellow precipitate, while aromatic and α,β-unsaturated aldehydes and ketones yield a orange-red precipitate).

## Physical Chemistry

### Experiment I.a: Initial rate method: Iodide-persulphate reaction

**Theory:**

Rate constant of a number of reaction involving ions in aqueous solution are highly influenced by the presence of inert electrolyte. This effect of ionic strength on the reaction rate is called primary kinetic salt effect.

Let us consider A and B ions react to form a product (P) through the formation of an activated complex ($X^{\neq}$),

$$A+B \rightleftharpoons X^{\neq} \rightarrow P$$

$$\text{Rate} = k'C_{x_{\neq}} \qquad \ldots\ldots\ldots\ldots \text{(i)}$$

Equilibrium constant ($K^{\neq}$) for activated complex,

$K^{\neq} = \frac{a_{X^{\neq}}}{a_A a_B} = \frac{C_{X^{\neq}}}{C_A C_B} \cdot \frac{f_{X^{\neq}}}{f_A f_B}$, where the terms have their usual significance.

Or, $C_{X^{\neq}} = K^{\neq} C_A C_B \frac{f_A f_B}{f_{X^{\neq}}}$

Substituting the value of $C_{X^{\neq}}$ in equation (i)

Rate = k' $K^{\neq} C_A C_B \frac{f_A f_B}{f_{X^{\neq}}} = k_0 \frac{f_A f_B}{f_{X^{\neq}}} C_A C_B$ …….. (ii), where $k_0 = k' K^{\neq}$,

the rate constant in absence of inert electrolyte.

Again the rate equation for this reaction (which is first order with respect to A and B each) can be represented as

Rate = $kC_A C_B$ …… (iii), where k is the experimentally found rate constant , comparing equation equation (ii) and (iii) we have

$K = k_0 \frac{f_A f_B}{f_{X^{\neq}}}$ or, $\log k = \log k_0 + \log f_A + \log f_B - \log f_{X^{\neq}}$……..(iv)

In the limit of sufficiently low ionic strength the activity coefficient of 'i'-th ion is related to the , ionic strength (I) of the solution as,

$\log f_i = -AZ_i^2\sqrt{I} = -0.509\, Z_i^2\sqrt{I}$ ,for aqueous solution at $25^0$C.

Therefore, equation (iv) can be written as

$\log k = \log k_0 - 0.509\, Z_A^2\sqrt{I} - 0.509\, Z_B^2\sqrt{I} + 0.509\, (Z_A + Z_B)^2\sqrt{I}$

$= \log k_0 + 1.018\, Z_A Z_B \sqrt{I}$

The plot of logk vs $\sqrt{I}$ gives a straight line having slope equals to $1.018\, Z_A Z_B$ with an intercept $\log k_0$.

Equation (v) represents the effect of ionic strength on the reaction rate.

**Three special cases may occur:**

1) If $Z_A$ and $Z_B$ have the same sign, then $Z_A Z_B$ is positive and the rate constant increases with ionic strength.

2) If $Z_A$ and $Z_B$ have different signs, $Z_AZ_B$ is negative and the rate constant decreases with ionic strength.
3) If one of the reactants is uncharged, $Z_AZ_B$ is zero and therate constant is independent of the ionic strength.

This change in k with ionic strength (I) is called primary kinetic salt effect. Ionic strength (I) of a solution is defined by

$I= \frac{1}{2}\Sigma C_iZ_i^2$ , where '$C_i$' is the concentration of the 'i' th ion in molality or molarity.

Effect of ionic strength on the rate and hence rate constant can be studied for the following reaction

$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

Experimentally this reaction is found to be first order with respect to $I^-$ and $S_2O_8^{2-}$ both. Rate of this reaction can be measured by following the rate of appearance of iodine. Here the iodine produced is made to react instantaneously with a fixed volume of thio-sulphate solution added to the reaction mixture until all the thio-sulphate is consumed (whereupon free iodine reacts with starch present in the solution to make it blue).

$$2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$$

By measuring the time taken for the known amount of thiosulphate to be consumed, the rate of production of iodine during that time can be calculated.

In this reaction, the iodine formed by the slow oxidation of persulphate is quickly reduced back to iodide by $S_2O_3^{2-}$ keeping the iodide concentration constant until the blue starch-iodine color appears. During this period apparent rate constant $k_{app}$ is given by

$$K_{app}= kC_{I^-} = \frac{Rate}{C_{S_2O_8^{2-}}} = \frac{C_{I_2}}{\Delta t \times C_{S_2O_8^{2-}}}$$

$$= \frac{Volume\ of\ S_2O_3^{2-}\text{-added (ml)} \times conc.of\ S_2O_3^{2-}\text{(N)} \times total\ volume\ (ml) \times 1000}{1000 \times total\ volume\ (ml) \times \Delta t \times Volume\ of\ S_2O_8^{2-}\ added\ (ml) \times conc.of\ S_2O_8^{2-}\ (N)}$$

$$= \frac{Volume\ of\ S_2O_3^{2-} added\ (ml) \times conc.of\ S_2O_3^{2-}(N)}{\Delta t \times Volume\ of\ S_2O_8^{2-} added\ (ml) \times conc.of\ S_2O_8^{2-}(N)}$$

From the experimental data apparent rate constant ($k_{app}$) and true rate constant (k) can be determined from the knowledge of $C_{I^-}$.

The effect of ionic strength on rate constant for this reaction can be studied by adding different concentration of inert electrolyte (say, $KNO_3$) to the reaction mixture.

**Apparatus required:**

1) 250ml volumetric flask -5
2) 250ml conical flask -6
3) Pipette- 10ml & 25ml (1 each)
4) Burette 50ml -1
5) 500ml Glass bottle -2
6) Stop watch

**Chemicals required**: KI, $Na_2S_2O_3$, $K_2S_2O_8$, $K_2Cr_2O_7$, Glacial acetic acid, 4(N) HCl, Starch.

**Procedure:**

1) Prepare 250ml ~ (N/10) $Na_2S_2O_3$ solution in a 500ml glass bottle.
2) Prepare 100ml ~ (N/10) $K_2S_2O_8$ solution in a 250ml glass bottle.
3) Prepare 250ml exact (N/10) KI solution by accurate weighing.
4) Prepare 250ml exact (N) $KNO_3$ solution by accurate weighing.
5) Prepare 100ml (N/10) $K_2Cr_2O_7$ solution by accurate weighing.
6) Standardize the ~ (N/10) sodium thiosulphate solution idometrically using starch solution as indicator. Take 10ml of standard (N/10) $K_2Cr_2O_7$ solution in a 500ml conical flask. Add about 15ml (one test tube) of ~ 10% KI solution and 20ml of 4(N) HCl solution. Cover the conical flask with watch glass and keep in dark for about 5 minutes. Add ~ 150ml of distilled water and titrate the liberated iodine with sodium thiosulphate solution using starch as indicator.
7) Prepare 250ml exact (N/100) $Na_2S_2O_3$ solution by proper dilution in a volumetric flask.
8) Take 25ml of exact (N/100) $Na_2S_2O_3$ solution in a 250ml volumetric flask, add deionized water up to the mark to prepare (N/1000) $Na_2S_2O_3$.

9) Standardize the prepared ~ (N/10) $K_2S_2O_8$ solution using the following procedure: Take 10ml of the prepared $K_2S_2O_8$ solution in a 250ml conical flask; add 20 ml of ~10% KI solution and 2ml of glacial acetic acid. Prepare two sets at the same time, cover the conical flask with watch glass and keep the mixture in dark for about 45 minutes. Add 50ml of water and titrate the liberated iodine against the standard thiosulphate solution using starch solution as indicator.

10) Prepared an exact (N/100) $K_2S_2O_8$ solution from the standardized $K_2S_2O_8$ solution by quantitative dilution (total volume 250ml).

11) Preparation of different sets (in 250ml conical flask) for the study of the effect of ionic strength on rate:

| Set | $10^{-1}$N KI (ml) | $10^{-3}$ $Na_2S_2O_3$ (ml) | 1 N $KNO_3$ (ml) | Deionized water(ml) | Starch (ml) | $10^{-2}$N $K_2S_2O_8$ (ml) |
|---|---|---|---|---|---|---|
| 1 | 20 | 10 | 0 | 44 | 1 | 25 |
| 2 | 20 | 10 | 1 | 43 | 1 | 25 |
| 3 | 20 | 10 | 3 | 41 | 1 | 25 |
| 4 | 20 | 10 | 5 | 39 | 1 | 25 |
| 5 | 20 | 10 | 10 | 34 | 1 | 25 |
| 6 | 20 | 10 | 20 | 24 | 1 | 25 |

12) Calculate $k_{app}$, k and $\sqrt{I}$ for each set.

Plot logk vs. $\sqrt{I}$ and explain the nature of the graph.(Determination $k_0$ from the intercept).

**Experimental Data:**

1) Room temperature:

2) Preparation of 250ml ~ 0.1 (N) sodium thiosulphate solution : Required weight = ~ 6.2g

3) Preparation of 100ml (N/10) $K_2Cr_2O_7$solution : Required weight =0.49

4) Standardization of $Na_2S_2O_3$ solution:

| Vol. of (N/10) $K_2Cr_2O_7$ solution (ml) | Burette reading | | Volume of $Na_2S_2O_3$ used (ml) | Average volume of $Na_2S_2O_3$ (ml) |
|---|---|---|---|---|
| | Initial(ml) | Final(ml) | | |
| 10 | | | | |
| 10 | | | | |

Strength of $Na_2S_2O_3$= ……..

5) **Preparation of 250ml exact (N/100) $Na_2S_2O_3$ solution:**

Required volume of prepared $Na_2S_2O_3$ solution =$\frac{250\times0.01}{Strength of Na_2S_2O_3 \text{ solution}}$ ml

…ml prepared $Na_2S_2O_3$ solution was taken (using burette ) in a 250ml volumetric fiask and rest of the volume was made by adding deionized water up to the mark.

6) **Preparation of 250ml exact (N/1000) $Na_2S_2O_3$ solution:**

25ml exact (N/100) $Na_2S_2O_3$ solution was taken in a 250ml volumetric flask and rest of the volume was made by adding deionized water up to the mark.

7) Preparation of 100ml ~ (N/10) $K_2S_2O_8$ solution in a 500ml glass bottle: Required weight =1.352g

8) Standardization of $K_2S_2O_8$ solution:

| Volume of $K_2S_2O_8$ solution (ml) | Burette reading | | Volume of $Na_2S_2O_3$ used (ml) | Average volume of $Na_2S_2O_3$(ml) |
|---|---|---|---|---|
| | Initial(ml) | Final(ml) | | |
| 10 | | | | |
| 10 | | | | |

Strength of $K_2S_2O_8$ solution =……..

## 9) Preparation of 250ml exact (N/100) $K_2S_2O_8$ solution:

Required volume of prepared $K_2S_2O_8$ solution $= \frac{250 \times 0.01}{Strength of K2S2O8 \text{ solution}}$ ml

…ml prepared $K_2S_2O_8$ solution was taken (using burette ) in a 250ml volumetric flask and rest of the volume was made by adding deionized water up to the mark.

## 10) Recording of time:

| Set | $\Delta t$(sec) | $C_{I^-}$(mole/lit) | $K_{app}$($sec^{-1}$) | K($mol^{-1}L\ sec^{-1}$) |
|---|---|---|---|---|
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |

**Calculation:**

Ionic strength of different sets:

| Set | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Ionic strength(I) | | | | | | |

$I=1/2\ \Sigma\ C_iZ_i^2$ , where '$C_i$' is the concentration of the 'i' th ion in molarity, $Z_i$ is the charge on the 'i' th ion.

| Set | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| logk | | | | | | |
| $\sqrt{I}$ | | | | | | |

**Conclusion**: Since here $Z_A$ and $Z_B$ have the same sign, then $Z_AZ_B$ is positive and the rate constant will increase with ionic strength which is found from the plot of log k vs. $\sqrt{I}$.

Also value of $k_0$=……

## Experiment I.b.i: Acid hydrolysis of methyl acetate with hydrochloric acid

**Theory:**

The acid catalyzed hydrolysis reaction of ester can be represented as

$$R_1COOR_2 + H_2O + H^+ \rightleftarrows R_1COOH + R_2OH$$

The rate equation is represented as

$$-\frac{d[R_1COOR_2]}{dt} = k[R_1COOR_2][H^+][H_2O]$$

$= k_1[R_1COOR_2]$, where $k_1 = k[H^+][H_2O]$ = constant, (in large excess of water,$[H_2O]$ remains constant and $H^+$ being the catalyst $[H^+]$ is constant)

Therefore the reaction becomes first order w.r.t ester. Integration of this equation with the boundary conditions, when t= 0, $[R_1COOR_2] = C_0$ and at time t, $[R_1COOR_2] = C$, gives

$$K_1 = (2.303/t)\log (C_0/C)$$

The progress of the catalyzed reaction may be studied by withdrawing measured volume of aliquot from the reaction mixture at different intervals of time and titrating with standard alkali solution using phenolphthalein indicator. The volume of alkali required at any instant is equivalent to be the sum of weak acid (produced as a result of hydrolysis) and the acid used as catalyst (a constant quantity).

If $V_0$, $V_n$ and $V_i$ be the volumes of alkali required for the same volume of aliquot at the beginning, at time t= $t_n$ and at the end of the reaction (at infinite time) respectively then,

$$C_0 \propto (V_i - V_0) \text{ and } C \propto (V_i - V_n)$$

$$\text{Then, } k_1 = \frac{2.303}{t_n} log \frac{(V\infty - V0)}{(V\infty - Vn)}$$

To avoid the measurement of $V_0$ the equation may be represented in the form

$\Delta t_n = t_n - t_1 = \frac{2.303}{k_1} log \frac{(Vi - V1)}{(Vi - Vn)}$

Where $V_n$ and $V_1$ are the volumes of alkali required at times $t_n$ and $t_1$ respectively.

Plot of $log \frac{(Vi - V1)}{(Vi - Vn)}$ vs $\Delta t_n$ will give a straight line passing through the origin and the slope $k_1$ may be determined by

$$K_1 = \text{slope} \times 2.303$$

**Apparatus required:**

1) 100 mL dry conical flask-1
2) 500 mL bottle for NaOH.
3) 2 mL pipette; 5 mL pipette-1 each
4) 250 mL conical flask-5
5) Sufficient ice cold water; water bath
6) Stop watch

**Chemicals required:** Methyl acetate, NaOH, and Phenolphthalein

**Procedure:**

1) Prepare 250 mL of approximately 0.1(N) NaOH solution.
2) Prepare 100 mL 1(N) HCl solution
3) Pipette out 50 mL of prepared HCl solution (catalyst solution) in a 100 mL dry conical flask, add 5 mL of ester using a pipette. Start the stop watch at the time of half discharge. Mix the solution thoroughly by swirling motion.
4) At 5-7 minutes intervals take 2 mL aliquot and add to 50 mL ice cold water taken in a 250 mL conical flask. Note the time of half discharge. Titrate rapidly against the prepared~ 0.1(N) NaOH solution taken in a burette, using phenolphthalein as indicator. Take at least 6 readings.
5) The remaining solution is heated at about 60ºC in a water bath~for 40 minutes with an air condenser fitted in the mouth of conical flask. The solution is allowed to cool to room temperature. Pipette out 2mL of it in 50 mL water taken in a 250 mL conical

flask and titrate with~0.1(N) NaOH solution; using phenolphthalein as indicator. The titre value correspond to $Vi$.

6) Plot a graph of $log\frac{(Vi-V1)}{(Vi-Vn)}$ vs $\Delta t_n$ and draw the best fit straight line passing through the origin.
7) Calculate the value of '$k_1$' from the slop of the graph.

**Experimental result:**

**1)** Room temperature
**2)** Preparation of 250 mL~0.1(N) NaOH solution: Dissolve 1 g NaOH in 250 mL deionized water.
**3)** Preparation of 100 mL 1(N) HCl solution: Dissolve~9mL conc. HCl in 91 mL deionized water
**4)** Recording of data for ester hydrolysis:

| Time(t) | Time($t_n$)in sec | $\Delta t_n = t_n - t_1$ | Volume of NaOH($V_n$mL) | ($V_i$-$V_1$) mL | ($V_i$-$V_n$)mL | $log\frac{(Vi-V1)}{(Vi-Vn)}$ |
|---|---|---|---|---|---|---|
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

**5)** Determination of $V_i$:
$V_i$ = Volume of NaOH required to standardize 2 mL reaction mixture after heating at about 60℃ in a water bath.

**6)** Plotting of graph:

| $log\frac{(Vi-V1)}{(Vi-Vn)}$ | | | | | | |
|---|---|---|---|---|---|---|
| $\Delta t_n$(Sec) | | | | | | |

**Calculation:** Observed rate constant, $k_1$=slope×2.303

**Conclusion:** Therefore observed rate constant for the acid catalyzed hydrolysis of methyl acetate at …..℃ is…..$sec^{-1}$.

## Experiment I.b.ii: Compare the strengths of HCl and $H_2SO_4$ by studying kinetics of hydrolysis of methyl acetate

**Theory:**

The acid catalyzed hydrolysis reaction of ester can be represented as

$$R_1COOR_2 + H_2O + H^+ \rightleftarrows R_1COOH + R_2OH$$

The rate equation is represented as

$$-\frac{d[R_1COOR_2]}{dt} = k[R_1COOR_2][H^+][H_2O]$$

$= k_1[R_1COOR_2]$, where $k_1 = k[H^+][H_2O]$ = constant, (in large excess of water,$[H_2O]$ remains constant and $H^+$ being the catalyst $[H^+]$ is constant)

Therefore the reaction becomes first order w.r.t ester. Integration of this equation with the boundary conditions, when t= 0, $[R_1COOR_2] = C_0$ and at time t, $[R_1COOR_2] = C$, gives

$$K_1 = (2.303/t)\log (C_0/C)$$

The progress of the catalyzed reaction may be studied by withdrawing measured volume of aliquot from the reaction mixture at different intervals of time and titrating with standard alkali solution using phenolphthalein indicator. The volume of alkali required at any instant is equivalent to be the sum of weak acid (produced as a result of hydrolysis) and the acid used as catalyst (a constant quantity).

If $V_0$, $V_n$ and $V_i$ be the volumes of alkali required for the same volume of aliquot at the beginning, at time t= $t_n$ and at the end of the reaction (at infinite time) respectively then,

$$C_0 \propto (V_i - V_0) \text{ and } C \propto (V_i - V_n)$$

Then, $k_1 = \frac{2.303}{t_n} log \frac{(V\infty - V0)}{(V\infty - Vn)}$

To avoid the measurement of $V_0$ the equation may be represented in the form

$$\Delta t_n = t_n - t_1 = \frac{2.303}{k_1} log \frac{(Vi - V1)}{(Vi - Vn)}$$

Where $V_n$ and $V_1$ are the volumes of alkali required at times $t_n$ and $t_1$ respectively.

Plot of $log \frac{(Vi - V1)}{(Vi - Vn)}$ vs $\Delta t_n$ will give a straight line passing through the origin and the slope $k_1$ may be determined by

$$K_1 = \text{slope} \times 2.303$$

**Apparatus required:**

7) 100 mL dry conical flask-1
8) 500 mL bottle for NaOH.
9) 2 mL pipette; 5 mL pipette-1 each
10) 250 mL conical flask-5
11) Sufficient ice cold water; water bath
12) Stop watch

**Chemicals required:** Methyl acetate, NaOH, and Phenolphthalein

**Procedure:**

8) Prepare 250 mL of approximately 0.1(N) NaOH solution.
9) Prepare 100 mL 1(N) HCl solution
10) Pipette out 50 mL of prepared HCl solution (catalyst solution) in a 100 mL dry conical flask, add 5 mL of ester using a pipette. Start the stop watch at the time of half discharge. Mix the solution thoroughly by swirling motion.
11) At 5-7 minutes intervals take 2 mL aliquot and add to 50 mL ice cold water taken in a 250 mL conical flask. Note the time of half discharge. Titrate rapidly against the prepared~ 0.1(N) NaOH solution taken in a burette, using phenolphthalein as indicator. Take at least 6 readings.

12) The remaining solution is heated at about 60ºC in a water bath for 40 minutes with an air condenser fitted in the mouth of conical flask. The solution is allowed to cool to room temperature. Pipette out 2mL of it in 50 mL water taken in a 250 mL conical flask and titrate with 0.1(N) NaOH solution; using phenolphthalein as indicator. The titre value correspond to $Vi$.

13) Plot a graph of $log\frac{(Vi-V1)}{(Vi-Vn)}$ vs $\Delta t_n$ and draw the best fit straight line passing through the origin.

14) Calculate the value of '$k_1$' from the slop of the graph.

**Experimental result:**

**7)** Room temperature

**8)** Preparation of 250 mL 0.1(N) NaOH solution: Dissolve 1 g NaOH in 250 mL deionized water.

**9)** Preparation of 100 mL 1(N) HCl solution: Dissolve 9mL conc. HCl in 91 mL deionized water

**10)** Recording of data for ester hydrolysis:

| Time(t) | Time($t_n$)in sec | $\Delta t_n = t_n - t_1$ | Volume of NaOH($V_n$mL) | ($V_i$-$V_1$) mL | ($V_i$-$V_n$)mL | $log\frac{(Vi-V1)}{(Vi-Vn)}$ |
|---|---|---|---|---|---|---|
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

**11)** Determination of $V_i$:

$V_i$ = Volume of NaOH required to standardize 2 mL reaction mixture after heating at about 60℃ in a water bath.

**12)** Plotting of graph:

| $log\frac{(Vi-V1)}{(Vi-Vn)}$ | | | | | | |
|---|---|---|---|---|---|---|

| | | | | | | |
|---|---|---|---|---|---|---|
| $\Delta t_n$(Sec) | | | | | | |

**Calculation:** Observed rate constant, $k_1$=slope×2.303

**Conclusion:** Therefore observed rate constant for the acid catalyzed hydrolysis of methyl acetate at …..℃ is…..$sec^{-1}$.

Repeat the same experiment with $H_2SO_4$ and compare the data.

**Experiment I.b.iii Study of kinetics of decomposition of $H_2O_2$.**

**Theory:**

The reaction between $H_2O_2$ and KI in dilute $H_2SO_4$ medium is represented as

$$H_2O_2+2KI+ H_2SO_4= I_2+2H_2O+ K_2SO_4$$

Suggested reaction mechanism is

$$H_2O_2+I^-= H_2O+OI^-….(slow)$$

$$OI^- +2H^++I^-= H_2O+I_2 \quad …….(fast)$$

The first step being the slowest step is the rate determining step. The differential rate becomes

$-\frac{d[H_2O_2]}{dt} = k[H_2O_2][I^-]$, where k is the rate constant and other terms have their usual significance.

Therefore kinetically the reaction is of second order (overall). But if the concentration of iodide ion is kept constant [by adding $Na_2S_2O_3$ continuously whereby the $S_2O_3^-$ ions react with the liberated iodine ($I_2$) and regenerate $I^-$ according to the equation, $I_2+2\ S_2O_3^{2-}= S_4O_6^{2-} +2I^-$] the reaction becomes kinetically first order w.r.t.[ $H_2O_2$] only. Under this condition the rate equation may be expressed as

$-\frac{d[H_2O_2]}{dt} = k_1[H_2O_2]$, where $k_1=k[I^-]$

If the initial (at time t=0) concentration of $H_2O_2$ is a and at time t, $[H_2O_2]$ = (a-x), (where, x= amount of $H_2O_2$ reacted), integration of the above equation gives

$$K_1=\frac{2.303}{t}\log\frac{a}{a-x}$$

If both 'a' and (a-x) are represented in terms of their $Na_2S_2O_3$equivalent , we have

$V_0 \propto a$ (where $V_0$ is the titre value of thiosulphate for the total iodine liberated by a fixed volume of $H_2O_2$ solution of concentration 'a' after complete decomposition).

And $V_t \propto x$ (where $V_t$ is the titre value of the same thiosulphate solution for the iodine liberated by the same $H_2O_2$ solution undergoing reaction at time t)

The rate equation may then be express as

$$K_1=\frac{2.303}{t}\log V_0/V_0-V_t$$

$$\text{Or, } \log V_0/V_0-V_t=k_1t/2.303$$

A plot of $V_0/V_0-V_t$ vs. t will give a straight line passing through the origin and from the slope $k_1$ may be determined, $k_1$= slope× 2.303.

**Apparatus required:**

1) 500 mL conical flask-2
2) 500 mL glass bottle for thiosulphate-1
3) Burette-1
4) 250 mL volumetric flask for KI-1
5) 10 mL pipette
6) Watch glass
7) Stop watch

**Chemicals required:**$H_2O_2$ , Sodium thiosulphate,KI,12N $H_2SO_4$,1% Ammonium molybdate solution, Starch

**Procedure:**

1) Prepare 100 mL '2 volume' $H_2O_2$solution. in a glass bottle.
2) Prepare 250 mL of 0.1(N) sodium thiosulphate solution in glass bottle. Fill the burette with sodium thiosulphate solution.
3) Take 10 mL 12 (N) $H_2SO_4$ in a 500 mL conical flask. Add 10 mL of prepared $H_2O_2$ solution followed by addition of 50 mL of water. Then add approximately 2 gm soli KI. Add 2 mL 1% ammonium molybdate solution. Cover the conical flask with a watch glass and keep it in dark for 1 minute. Add about 50 mL of water and titrate the liberated iodine with sodium thiosulphate solution using starch as indicator. Record the volume of thiosulphate ($V_0$).
4) Take 250 mL of 0.4% KI solution (dissolve 1 gm KI in 250 mL deionized water) in a 500 mL conical flask. Add 15 mL 12(N) sulphuric acidand 5 L of freshlypreparedstarch solution. Add 10 mL of prepared $H_2O_2$ solutions and at the time of half discharge start stop watch.

   Run immediately sodium thiosulphate solution from the burette from the burette into the mixture in excess to discharge the blue colour. Wait for appearance of blue colour and record the time (t) of reappearance of colour, volume of thiosulphate used ($V_t$).

   Again run thiosulphate into the mixture in excess to discharge the blue colour, record time (t) of reappearance of colour, and total volume of thiosulphate used ($V_t$).Take at least 6 readings.
5) Plot log $[V_0/(V_0-V_t)]$ vs. t in millimeter graph paper and draw the best fit straight line passing through the origin. Calculate '$k_1$' value from the slope of the graph.

**Experimental result:**

1) Room temperature
2) Preparation of 250 mL~ 0.1(N) sodium thiosulphate solution: Dissolve~ 6.2 gm $Na_2S_2O_3$ in 50 mL deionized water.
3) Determination of $V_0$ :

   $V_0$ = titre value of thiosulphate for the total iodine liberated by 10 mL of''2 volume'$H_2O_2$ solution after complete decomposition.

**4) Titre value of thiosulphate at different times:**

| Time(t) | Time (t) in sec | Volume of $S_2O_3^{2-}$ used ($V_t$ mL) | $(V_0-V_t)$ mL | $\log V_0/V_0-V_t$ |
|---|---|---|---|---|

**5) Plotting of graph:**

$\log V_0/V_0-V_t$

t(sec)

**Calculation:**Observed rate constant, $k_1$=slope× 2.303

**Conclusion:**Therefore observed rate constant for the decomposition of $H_2O_2$ at ….. ºC is …….$Sec^{-1}$.