Organic Functional Group Analysis

A functional group is a specific group of atoms within a molecule that is responsible for characterstic chemical reactions of that molecule.

Functional group is an atom (or) group of atoms attached to the given organic compound.

⇒ Functional group is responds to the organic compounds containing Hetero atoms.

⇒ Generally organic compounds contain carbon and Hydrogen. In addition to these elements they may contain other atoms like halogens, Oxygen, Nitrogen and Sulphur.

⇒ "The organic compounds containing hetero atoms imparts basic (or) acidic (or) Neutral character to the organic compound more groups which changes the nature of hydro carbons are said to be functional group."

classification :-

Functional groups are classified into three categories basing on their solubility

1. Acid compounds / Acidic functional group
2. Basic compounds / Basic functional group
3. Neutral compounds / Neutral functional group

1. Acid compounds :-

The organic compounds which donates H^+ ions are called acid compounds functional groups with acidic nature are carboxylic acid, phenol, endiol, enols, thiols or mercaptions etc.

2. Basic compounds :-

The organic compounds which accept H^+ ions are called basic compounds. Functional groups with basic nature are Amines (aliphatic & aromatic) hydrazine derivatives.

3. Neutral compounds :-

The organic compound which neither donate nor accept H^+ ions are called neutral compounds. functional group with neither acid nor basic nature are aldehydes, ketones, nitrogroup ($-NO_2$), Methoxy ($-OCH_3$) and Olefinic group.

Acidic functional Group Analysis

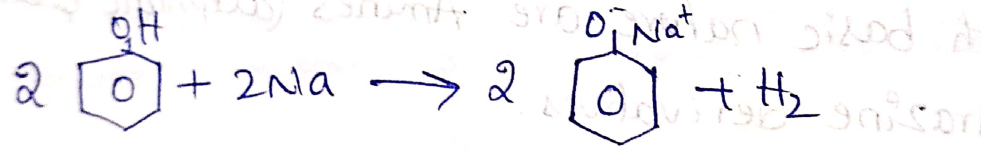
1. Determination of phenolic Hydroxyl compounds : (Phenol)

Phenol :- The simplest aromatic hydroxy compound is C_6H_5OH.

⇒ phenols are relatively more soluble in water due to their ability to form hydrogen bonding with water molecules.

⇒ Alcohols and phenols react with active metals like Na, K (or) Al to yield alkaoxides / phenoxides and hydrogen.

$$2R\text{-}OH + 2Na \longrightarrow 2R\text{-}ONa + H_2$$



phenol — Sodium phenoxide

⇒ The phenolic group and the phenolate ion in a molecule exhibit strong electron donating effects that make the simple phenolic compound readily undergo electrophilic substitution reaction with strong electrophilic agents such as nitroso group and diazonium salt. Substitution is

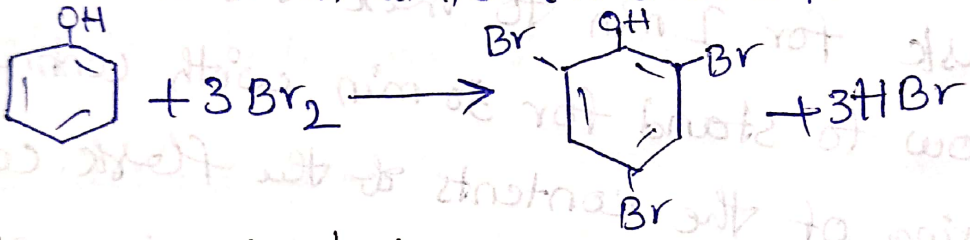
directed to para or ortho to the hydroxyl group.

Many of the substituted phenols are highly colored; therefore the substitution reactions are used for the analysis.

Estimation of phenols by Bromination method :-

principle :- $KBrO_3 + 5KBr + 6HCl \rightarrow 3Br_2 + 6KCl + 3H_2O$

In Bromination method, the sample is treated with $KBrO_3$-KBr solution under acidic conditions to form 2,4,6-tri bromo phenol.



Solutions Required :-

1. **0.2 N Potassium Bromate-Bromide Solun :-**

Dissolve 5.567 g of A.R potassium bromate and 7.5 g of pure potassium bromide in water and dilute to 1 lit in a volumetric flask.

2. **0.1 N Hypo :-**

Dissolve about 25 g of AR Sodium thiosulphate in 1 lit of freshly boiled & cooled distilled water std by KIO_3.

3. 20% KI

4. Starch

Procedure :-

weighout accurately about 0.25gm Phenol, dissolve in 5ml of 10% NaOH solution, and dilute the solution to 250 ml in a V.f. pipette out the 25 ml of the phenol solution into a 500ml iodine flask, followed by 25ml of the bromate-bromide solution and dilute with 25 ml of water. Add 5 ml of conc. HCl & stopper the flask immediately shake the flask for 1 min to mix the reactants and allow to stand for 30 min with continuously stirring of the contents of the flask. Cool the flask under the tap or ice water. Add 10ml of 20% KI solution in the cup around the stopper. Slightly remove the stopper where upon the I_2 solution is liberated. The I_2 is titrated with std. Hypo solution until yellow colour is obtained. then add starch indicator & continuously titrated with hypo until blue colour is obtained. Blank titration same as procedure.

$$\% \text{ of purity} = \frac{(V_2 - V_1) \times M \times N \times 100}{W \times 1000 \times Z}$$

V_2 = vol. of Hypo for sample
V_1 = vol. of Hypo for blank
N = Normality of Hypo
M = M.wt of the sample
W = wt of the sample taken
Z = no. of bromins attached to the phenol group.

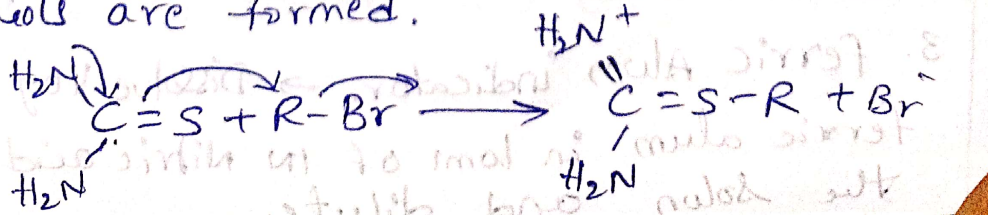
2. Determination of Thiols (Mercaptants) :- (R-SH)

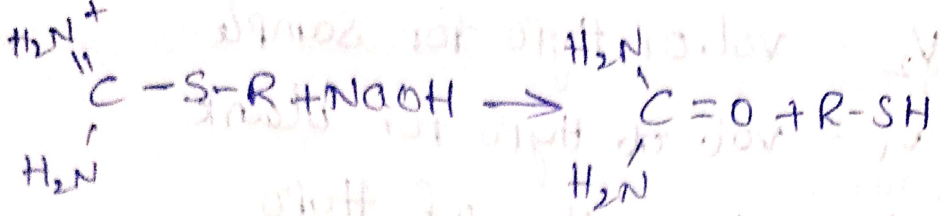
Thiols :- Thiols are the sulphur analogus of the alcohols and are formally called "Mercaptans" they exhibit acidic in nature these are prepared by following way.

1. Alkyl halides are treated with sodium hydro sulphide in presence of ethanolic solution then Thiols are formed.

$$R\text{-}Br + NaSH \xrightarrow{EtOH} R\text{-}SH + NaBr$$

2. when an alkyl bromide is treated with thio urea to form S-alkali thio uranium salts followed by hydrolysis with sodium hydroxide Thiols are formed.





⇒ Thiols smell bad.

⇒ Thiols are more acidic than alcohols

⇒ Many thiols are colourless liquids.

⇒ Thiols are mainly used for drugs & Pesticides.

Determination of Thiols :-

Thiols are determined by 2 methods.

1. Argentometric Method
2. Iodometric Method.

i) Determination of Thiols by the Argentometric Metho

Principle :- The sample is taken and $AgNO_3$ reagent are added to titrated with NH_4SCN by using ferric alum indicator to form a silver thiols.

$$R\text{-}SH + AgNO_3 \xrightarrow[Fe(III)]{NH_4SCN} Ag\text{-}SH$$

Solutions Required :-

1. 0.05 N $AgNO_3$ solution
2. 0.05 N NH_4SCN
3. Ferric Alum indicator. → Dissolve 4.0g of ferric alum in 10ml of 1N Nitric acid boil the solun and dilute.

Procedure :-

weigh out accurately 1-2 milli equivalents of the mercaptants dissolved it in 100ml of pure benzene. Pipette out 10ml of this solution into 250ml conical flask containing 10ml of anhydrous methanol add about 45ml of 0.005N $AgNO_3$ solution from a burette to the sample solution, the resultant solution is shaken vigorously. Then add 2ml of ferric alum indicator and titrate the solution with 0.05N Ammonium thio cyanate until a faint pink color is observed.

$$\%\text{ of Thiol} = \frac{V \times N \times 33.07}{W \times 1000} \times 100$$

V = Volume of $AgNO_3$ solution used for sample

N = Normality of $AgNO_3$ solution

W = weight of the sample taken.

ii) Iodometric Method :-

1. Iodine solution (0.1N) :- Dissolve 20g of Iodate free Potassium iodide solution in 30-40ml of water in 1 liter volumetric flask

2. Hypo solution : Dissolve 25 g of AR Hypo in 1 Liter of distilled water.

3. Starch indicator.

Procedure :-

weigh out accurately 0.2 gm of the mercaptans in a sealed glass ampoule and place in 500 ml Iodine flask, with a few glass beads it is used to breale the ampoule. Pipette out 50 ml of the standard 0.1 N Iodine solution into the flasks stopper the flask and shalce vigorously to breale the ampoule. and then allow to stand for 5 min. 20 ml of excess I_2 added to this solution and shalce again for 10-15 minutes. Titrate the excess of iodine with Std. 0.1N Hypo solution using starch indicator near the end point. Run a blanle determination using same procedure.

$$\% \text{ of Thiol} = \frac{(V_1 - V_2) \times N \times M}{W \times 1000} \times 100$$

V_1 = Volume of Hypo for sample

V_2 = Vol. of Hypo for Blank

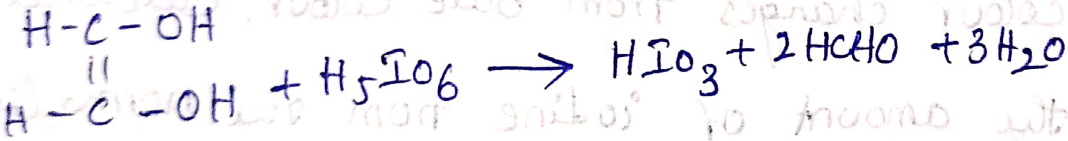
N = Normality of $Na_2S_2O_3$ (Hypo)

M = M.wt of the Mercaptans (33.07)

w = wt of the sample.

3. Determination of Ene-Diol :-

Principle :- Ene diols are oxidised quantitatively at ordinary temperature by excess of periodic acid (or) it's salts the remaining unreacted per iodic acid is back titrated with std. hypo solution and presence of starch as an indicator.



Solutions Required :-

1. Per iodic acid :-

Prepared (0.5 N) per iodic acid by dissolving required amount of distilled water filtered through a filtered glass funnel.

2. 0.2 N Hypo

3. 20% KI Solution

Procedure :-

weigh out accurately about 1.2 gm of Sample and dissolve in distilled water and make up to 250 ml volumetric flask. Transfer the 25 ml of the solution into 500 ml iodine flask and add 50 ml per iodic acid solution and mix the solution well, allowed to stand for 30 min. and add 30 ml of 20% KI followed by 25 ml of 6N H_2SO_4 titrate the solution with 0.2 N Hypo until pale yellow colour is obtained then add 2ml of starch indicator and continue the titration until the colour changes from blue colour. Calculate the amount of iodine from the normality and volume of Hypo consumed. Blank experiment is also perform.

$$\% \text{ of Iodine} = \frac{(V_2 - V_1) \times N \times M}{w \times 1000} \times 100$$

V_2 = volume of Hypo for sample

V_1 = volume of Hypo for blank

N = Normality of Hypo

M = M.wt of Iodine

w = wt of the sample

Basic Functional Group Analysis

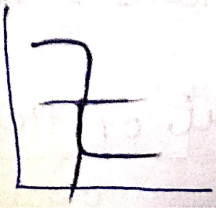
1. Determination of Mixture of 1°, 2°, 3° Amines :-

Solutions Required :-

1. 1:1 Mixture of ethylene Glycol and Isopropanole
2. 1N HCl
3. Acetic anhydride
4. Salicylaldehyde

Procedure (A) :- (Total Amines) :-

A sample containing 0.02 moles of Mixture of amine are accurately weighed and it is taken in a 150 ml beaker. This is diluted to 50 ml with 1:1 mixture of ethylene Glycol and Isopropanol and shaken which is under dissolution. The solution contain beaker is attached to the pH meter. Insert 1 combine glass electrode, Add 1N HCl from the burette make pilot titration. After pilot titrate make accurate titration take the jump after neutralization Plot a graph between pH and volume of HCl.



Moles of Total Amines / per gram of the sample ($1^{0}+2^{0}+3^{0}$) = $\frac{\text{ml. of HCl} \times \text{Normality of HCl}}{w \times 1000}$

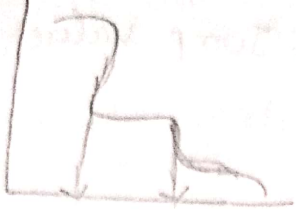
ml. of HCl → Jump value from graph

Procedure (B) :- [$2^{0}+3^{0}$ Amines]

A Sample containing 0.02 moles of 2^{0} & 3^{0} amin are accurately weighed in a weighing bottle. This is taken in a 150 ml beaker and diluted to 50 ml with 1:1 Mixture of ethylene Glycol and Isopropanol, shaken which is under dissolution the beaker is attached to the pH meter. Insert combine glass electrode, Add 1N HCl from the burette make a Piolet titration 1st jump is observed and add few ml of Salicylaldehyde and continue the titration we observed another jump (2nd jump) in titration.

Moles of $2^{0}+3^{0}$ Amines / grams of Sample = $\frac{\text{ml. of HCl} \times \text{N. of HCl}}{w \times 1000}$

ML of HCl = 2nd Jump value from graph.



Procedure (C) :- [3° Amines]

A Sample that contains approximately 0.02 moles of 3° Amine is weighed in a 20/150 mm test tube and is cooled by placing in a beaker of ice, two milli liters of acetic anhydride is added slowly while the test tube is swirled. The test tube contains are allowed to stand for 15 min at room temperature. The contents are quantitatively transferred from the test tube into 150ml beaker by washing with 1:1 Mixture.

1:1 Mixture is added untill the volume is 50 ml a pH meter is used to indicated the apparent pH after each addition of ~~water~~ acid as the sample is titrated with IN HCl prepared in the 1:1 Mixture the neutralization point is determined by plotting the apparent pH aganist Milli liters of acid.

$$\text{Moles of 3° Amine / grams of sample} = \frac{\text{ml. of HCl} \times \text{N. of HCl}}{w \times 1000}$$

ml of HCl → Jump value from graph.

Calculation :-

1. 1° amine :-

Moles of Total amines − Moles of (2°+3°) Amines

% of 1° Amine = Moles of 1° Amine x M.wt of 1° amine x 100

2° Amine :-

Moles of 2° Amine = Mole of (2°+3° Amine) − Moles of 3° amine

% of 2° amine = Mole of 2° amine x M.wt of 2° amine x 100

3° Amine :-

% of 3° amine = Moles of 3° Amine x M.wt of 3° Amine x 100

2 Determination of Aromatic Amines :-

Aromatic Amines are determined by two methods.

1. Bromination method 2. Diazotization Method.

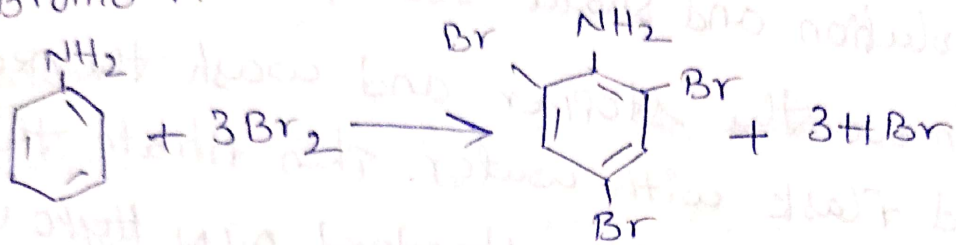
Bromination Method :-

Amines can be determined by Bromination.

⇒ Bromination with excess of standard Bromate - bromide solution in presence of HCl.

$KBrO_3 + 5\,KBr + 6HCl \rightarrow 3Br_2 + 6KCl + 3H_2O$

Then bromine reacts with aniline to form tri Bromo Aniline.



Reagents :-

1. Brominating Mixture
2. Hypo
3. KI
4. Starch

Procedure :-

Weigh out accurately about 0.25 g of the amine into a 250 ml V.F dissolved the sample in the minimum volume of dil.HCl and dilute to the mark with distilled water. Take 25ml of the amine solution into a 500 ml Iodine flask followed by 25 ml of the Bromate-Bromide solution and dilute with 25 ml of water. Add 5 ml of con.HCl and stopper the flask immediately. Shake the flask for 1 min to mix the reactants and allow to stand for 10 min cool the flask in ice water and

also place 10 ml of KI solution in the cup around the stopper and mix the solution and shake the flask for 30 min remove the stopper and wash the neck and flask with water. Then titrate the free iodine with standard 0.1N Hypo using 2ml of starch indicator until colour changes from blue to colorless. The same procedure is repeated with blank.

$$\% \text{ of Aniline} = \frac{(V_1 - V_2) \times N \times M}{W \times 1000 \times 2} \times 100$$

(ii) Diazotisation method (or) spectrophotometric.

Principle :-

Method :-

The amine is diazotised and then coupled with NEDA. This leads to the formation a coloured product whose concentration can be determined with a Spectrophotometer.

Solutions required :-

1. NEDA — N (1-napthyl) Ethyline Diamine Dihydrochloride.

0.3 gm of solid dissolved in 100 ml of 1% HCl.

2. 1M HCl

3. $NaNO_2$:- 0.7 gm of solid dissolve in 100 ml of water.

4. 90 % ethanol.

Procedure :-

weigh out 10-15 mg of the sample dissolved in 1 M HCl in a volumetric flask. Place 20ml of this solution in a conical flask and add 1 ml of $NaNO_2$ solution allow to stand for 5 min. Now add few ml of 90 % ethanol and after waiting a further 3 min, add 2ml of NEDA solution. A red colour develops rapidly, a blank solution containing all reagents except the amine. The measurement should be made at a wavelength of about 550nm. A calibration curve is prepared by using a series of solutions of pure amine of appropriate concentrations which are treated in the manner described above.

3. Determination of Hydrazine :-

Idometric Method :-

The sample is dissolved in 50 ml water then add few gm of $NaHCO_3$ and the solution is titrated with 0.1N iodine using starch as indicator.

% of Hydrazine =

$$\frac{\text{Vol. of iodine} \times \text{N. of } I_2 \times \text{M.wt of Hydrazine}}{w \times 1000} \times 100$$

Neutral Functional Group Analysis

1. Determination of Nitro group :-

Principle :-

Conversion of Nitro group into amine group by using selecting reducing agents like $SnCl_2$, $TiCl_3$, $Ti_2(SO_4)_3$ etc.

$$R\text{-}NO_2 \xrightarrow[\text{Reducent agent}]{[H]} R\text{-}NH_2$$

i) $Ti_2(SO_4)_3$ (Titanium sulphate) Method :-

Principle :- Aliphatic and aromatic nitro compounds can be reduced quantitatively using Ti^{3+} ion as a reducing agent in acidic medium the nitro group is reduced to amino group using 6 moles of Titanium ions.

$$R\text{-}NO_2 + 6\,Ti^{3+} + 6H^+ \longrightarrow R\text{-}NH_2 + 6\,Ti^{4+} + 2H_2O$$

Excess of Titanium salt can be determined by titrating against ferric ammonium sulphate solution using NH_4SCN as an indicator.

$$Ti^{3+} + Fe^{+3} \longrightarrow Ti^{+4} + Fe^{+2}$$

procedure :-

weigh out accurately, a dry sample containing about 0.015 gm of Nitrogroup into the flask, dissolve in few ml of water. Add 10 ml of dil. H_2SO_4 pass CO_2 gas through the flask for 5 min to remove O_2 (or) Air. Add excess of 50 ml of 0.1 N titanium sulphate solution and boil for 5-10 min to maintain the current inert gas cool to 35°-45° add 10 ml of NHyscN as indicator and titrated with standard 0.1N ferric ammonium sulphate solution untill end point pale red colour is obtained.

⇒ Blank is also determined as same procedure without sample.

$$\% \text{ of } NO_2 \text{ group} = \frac{(V_2 - V_1) \times N \times M}{W \times n \times 1000} \times 100$$

V_2 = volume of fe(III) for sample

V_1 = volume of fe(III) for Blank

N = Normality of fe (III)

M = M.wt of NO_2 group (46)

W = weight of the sample taken

n = no. of nitro groups attached to the compound.

ii) $SnCl_2$ Method :-

Principle :- Nitro group present in the sample is treated with $SnCl_2$ and HCl to get a amine and unreacted $SnCl_2$ and Tintetrachloride.

The unreacted $SnCl_2$ is treated with KI to form a Iodine to this 2ml starch is added and titrated with hypo to determine the nitro group.

$$SnCl_2 + 2KI \longrightarrow I_2 + 2KCl + SnCl_4$$

Solutions Required :-

1. $SnCl_2$ solution 2. HCl 3. 0.1N Hypo
4. Starch 5. 15% KI Solution

Procedure :-

0.015gms of Nitro group present in the sample taken in a titration flask, dissolve in few ml of water add 10ml dil. HCl pass CO_2 through the flask and heated at 35°-45°c to form an amine and $SnCl_4$ and unreacted $SnCl_2$ are also obtained.

$$R\text{-}NO_2 + SnCl_2 \xrightarrow{H^+} R\text{-}NH_2 + SnCl_4 + \underset{\text{unreacted}}{SnCl_2}$$

The unreacted $SnCl_2$ reacted with KI to liberate I_2.

$SnCl_2 + 2KI \longrightarrow I_2 \downarrow + 2KCl + SnCl_4$

The liberated iodine can be titrated with Std. 0.1N Hypo solution using starch indicator. The amount consume thiosulphate by iodine we can calculate the amount of sample. end point is blue to colourless.

Blank determination done by same procedure without sample.

$$\%\ \text{of purity}_{\text{Nitro group}} = \frac{(V_2 - V_1) \times N \times M}{w \times n \times 1000} \times 100$$

V_2 = volume of Hypo for sample

V_1 = volume of Hypo for Blank

N = Normality of Hypo

M = M.wt of NO_2 (46)

w = wt of Sample taken

n = no. of NO_2 groups attached.

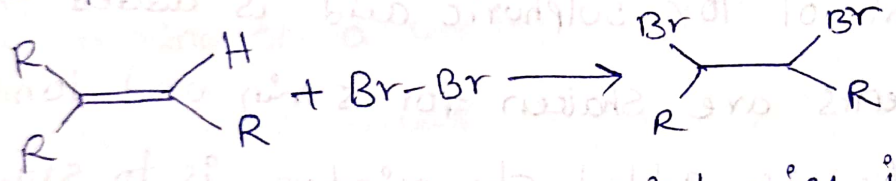
Determination of Olefinic group :-

i) Bromination Method :-

The bromination of the double bond forms basis of this Method. The bromine required for the reaction is generated from Potassium bromate in presence of $HgSO_4$ as a catalyst.

$$KBrO_3 + 5KBr + 3H_2SO_4 \xrightarrow{HgSO_4} 3Br_2\downarrow + 3K_2SO_4 + 3H_2O$$

The liberated bromine is reacted with double bond present in a sample is as follows.



The excess of bromine is determine iodometrically.

$$Br_2 + 2KI \longrightarrow 2KBr + I_2$$

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

Reagents :-

1. $KBr + KBrO_3$ solution :- Dissolve 2.73 gm of $KBrO_3$ and 30 gm of KBr in distilled water and diluted to 1 litre.
2. $HgSO_4$ (catalyst) :- 12 g of mercuric Solphate dissolved in a solution of con H_2SO_4 and 380 ml of distilled water.
3. 0.05 N Hypo

4. KI
5. H_2SO_4 [10%]
6. 2N NaCl
7. Starch indicator

Procedure :-

Weighed ~~accur~~ accurately 0.1 - 0.2 g of the given compound. It is dissolved in 25 ml water or CCl_4 in an iodine flask. Then add 25 ml of Bromate - Bromide solution and add 20 ml of 10% sulphuric acid is added. Then the contents are shaken for 5 min and 10 ml H_2SO_4 solution is added. The mixture is to stand for 7 - 10 min with shaking then add 15 ml of 2N NaCl is added to liberate free bromine from the mercuric sulphate complex followed by addition of KI. The flask is shaken for 1 min and liberated iodine is titrated with 0.05N hypo using starch as indicator run a blank determination under the same experimental condition as the sample.

$$\% \text{ of Olefinic} = \frac{(V_2 - V_1) \times N \times M}{W \times n \times 1000} \times 100$$

V_2 = volume of Hypo for sample

V_1 = volume of Hypo for Blank

N = Normality of Hypo

M = Molecular weight of Olefinic group

n = no. of bromine attached to the given organic compound.

ii) Wij's Method :- (Wij's Method)

Reagents :-

1. Wij's Solution :- Dissolve 7.9 gms of ICl_3 and 8.7 gms of I_2 in Glacial acetic acid by warming on a water bath. mix the two solutions and dilute to 1 liter with glacial acetic acid. Store the wij's solution in a amber bottle.
2. KI [15%]
3. 0.1 N Hypo
4. Starch indicator

Procedure :-

weigh accurately 0.1 - 0.5 g of the sample in a glass stopper flask dissolve the sample in 10 ml CCl_4 or $CHCl_3$ warm slightly. now add 25 ml of the wij's solution and 20 ml of KI and 100 ml of water, stopper the flask, shake and allow to stand in the dark for 30 min.

Then iodine is liberated. The iodine is titrated with standard 0.1N Hypo using starch as indicator until the colour changes from blue to colourless.

$$\% \text{ of Olefinic} = \frac{(V_2 - V_1) \times N \times 12.692 (M)}{w \times 1000} \times 100$$

V_2 = volume of Hypo for sample

V_1 = volume of Hypo for Blank

N = Normality of Hypo

w = wt of the sample taken

M = Molecular weight of Olefinic group

iii) Hanu's Method :-

Reagents :-

1. Hanus Solution :- 20 gm of IBr dissolved in 1 litre of Glacial acetic acid.

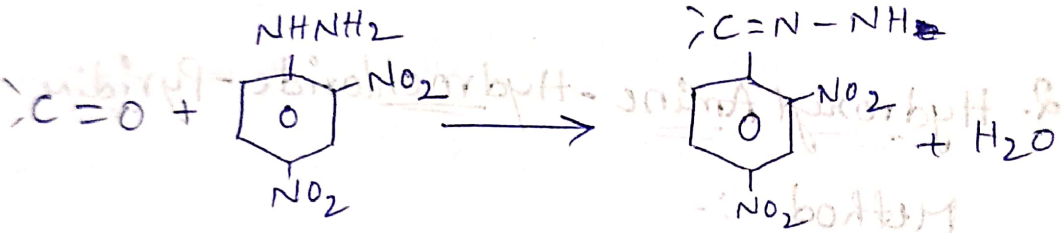
Procedure :- Same as Wij's Method.

3. Determination of carbonyl group (>C=O)

1. 2,4 - DNPH Method :-

Principle :- 2,4 DNPH reacts with carbonyl compounds and forms a ppt of 2,4-Dinitro phenyl hydrazone which is filtered, dried and weighed.

>C=O + 2,4-DNphydrazine → 2,4-DNP hydrazone.



Solutions Required :-

1. 2,4-Dinitrophenyl Hydrazine
2. 2N HCl

Procedure :-

Place 50 ml of 2,4-DNPH reagent in 250 ml conical flask and accurately weighed quantity of carbonyl compound is added the flask is shaked well for 15 min and allowed to stand in a ice bath for 1 hour with occasional shaking. The precipitate is formed. The precipitate is filtered in preweighed sintered crucible and washed with 2N HCl followed by water. The crucible is dried

in oven finally to get a constant weighed.

$$\% \text{ of } >C=O = \frac{W \times F}{w} \times 100$$

where,

W = weight of 2,4-DNPH

F = Gravimetric factor

w = weight of the sample taken

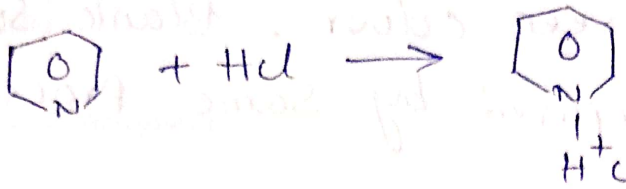
2. Hydroxyl Amine-Hydrochloride-Pyridine Method :-

Principle :- The method is based on the reaction of the carbonyl compound with hydroxyl amine hydrochloride to form oxime in the presence of pyridine.

$$>C=O + NH_2OH.HCl \xrightleftharpoons{\text{Pyridine}} >C=N-OH + H_2O + HCl$$

(oxime)

The reaction is reversible and the equilibrium is shifted towards the right hand side on addition of pyridine. Pyridine forms Pyridinium hydrochloride with HCl.



Pyridinium hydrochloride is acidic and it is titrated with standard NaOH by using Bromophenol Blue indicator.

Solutions Required :-

1. 0.5 N NH_2OH-HCl :- Dissolve 17.5 gm of Pure $NH_2OH.HCl$ in distilled water and dilute to 500 ml with 95% ethanol.
2. NaOH :- Dissolve 19 gm of NaOH pellets in distilled water.
3. Bromo phenol blue indicator.

Procedure :-

Accurately weighed carbonyl compound Sample is taken in glass stoppered flask and add 30 ml of $NH_2OH.HCl$ solution and 10 ml of bromo phenol blue indicator allow to stand for 30 min and the solution is refluxed on a steam bath for 2hr the resulted solution is titrated with Standard NaOH solution becomes

Blue to green colour. Blank solution can be prepared by same procedure without sample.

$$\% \text{ of carbonyl compound} = \frac{(V_2 - V_1) \times N \times M}{w \times 1000} \times 100$$

V_2 = Volume of NaOH for sample

V_1 = Volume of NaOH for Blank

N = Normality of NaOH

M = Molecular weight of the compound

w = weight of the sample taken.

4. Determination of Methoxy group ($-OCH_3$) :-

Zeisel's Method :-

Principle :- A known weight of substance is decomposed by heating with constant boiling hydro Iodic acid it gives volatile Methyl Iodide.

$$R\text{-}OCH_3 + HI \longrightarrow CH_3I + R\text{-}OH$$

$$CH_3OH + HI \longrightarrow CH_3I + H_2O$$

The evaluted volatile methyl Iodide can be estimated either Gravimetrically or volumetrically.

i) Gravimetric Method :-

In this Gravimetric Method, few ml of given sample and few ml of HI taken in a flask. The above solution is boiled. Through the boiled solution pass CO_2 gas for evolution of CH_3I. Evoluted CH_3I is transferred to an Absorption flask containing 4% alcoholic solution of $AgNO_3$ The $AgNO_3$ reacts with CH_3I to form AgI precipitate. The precipitate is filtered and washed with dil. HNO_3/ H_2O. Then dried and finally weighed.

$$\% \text{ of Methoxy group} = \frac{\text{wt of AgI} \times \text{Gr.f}}{\text{wt of sample}} \times 100$$

ii) Volumetric Method :-

In this method methyl iodide formed in the reaction is absorbed in an acetic acid solution of sodium acetate containing bromine solution. Under these conditions iodine mono bromide is first formed which is further oxidized to Iodic acid.

$$CH_3I + Br_2 \longrightarrow CH_3Br + IBr$$

$$IBr + 2Br_2 + 3H_2O \longrightarrow HIO_3 + 5HBr$$

The Iodic acid is then determined iodometrically adding KI solution followed by dil. H_2SO_4. The iodine is titrated with Hypo. Excess of Br_2 is removed from the reaction mixture by the addition of formic acid.

$$Br_2 + HCOOH \longrightarrow 2HBr + CO_2$$

$$HIO_3 + 5KI + H_2SO_4 \longrightarrow 3I_2$$

$$3I_2 + 6Na_2S_2O_3 \longrightarrow 3Na_2S_4O_6 + 6NaI$$

Solutions Required :-

1. Sodium acetate solution
2. KI Solution (5%)
3. Hypo (0.05N)
4. Starch
5. 10% H_2SO_4
6. HI
7. Bromine/AcOH
8. 98% HCOOH

Procedure :-

Accurately weighed 5-10 mg of sample taken into Reaction flask, to this 3-4 drops of acetic anhydride is added and shake to dissolve the sample and create inert atmosphere by passing CO_2 gas and 5ml HI is passed through the reaction mixture. The flask is gently heated at 125 to 130°c for an hour. Then the solution is transferred into Iodine flask after washing with sodium acetate solution, the flask is shaken and allowed to stand for 2-3 min then KI is added followed by 10 ml of 10% H_2SO_4, boiled and add few ml of HCOOH allowed to stand for 5-10 min then I_2 is liberated. The liberated I_2 is titrated with Hypo using starch as indicator.

Blank experiment is also performed without sample.

$$\% \text{ of Methoxy group} = \frac{(V_2 - V_1) \times N \times M}{w \times 1000} \times 100$$

V_2 = volume of Hypo for sample

V_1 = volume of Hypo for blank

N = Normality of Hypo

M = Molecular weight of given compound

w = weight of the sample.