"Microscale Experiments in Organic and Inorganic Chemistry"

DEPARTMENT OF CHEMISTRY

S.T. HINDU COLLEGE

(Re-accredited by NAAC with 'A')

NAGERCOIL - 629 002.

Semimicro Preparations and Capillary reactions

The rising cost of chemicals and decreased flow of funds are causing great concerns to the chemistry teachers. A tug - of - war had also been going on in recent years, to balance the budget of running practical courses and the standards of experiments to be carried out by the students. Since the economy is always the winner, the number of experiments had been the losers.

A group of scientists from University of Pune and Fergussion College, Pune are striving hard to maintain the standards of experiments at a friendly budget ie., by adopting to preparations on a micro scale and carrying out reactions in capillaries / tiles.

Their attempts serve many purposes.

(i) cuts down the cost of chemicals.

(ii) experiments have become environment friendly.

(iii) less time consuming

(iv) less hazardous to the teachers, students and lab, assistants. What more it becomes affordable.

Microscale Preparations

To do preparations on a microscale, we need10ml/ 5ml R.B. flasks. B_{10} water condensers. The advantages of having the miniature apparatus are many. We can save on fuels as well as chemicals. When we use the B_{10} water condenser, we can connect the inlet and outlets by a rubber tube, so that there is no need for running water. As the amount of heat supplied is less, the water in the condenser itself serve the purpose of cooling most of the time. So we save on the use of water, consequently on electricity (as there is no need for overhead tank waer for circulation). As the preparations are done on a microscale, it is enough if we make use of small size filter papers. Filtration can be fast, there also we save on the consumption of filter paper and electricity. Recrystallisation done on microscale leads to savings on the solvent front.

Less usage of chemicals, so less toxic emission and so it becomes environment friendly. Overall the microscale preparations have so many advantages over the conventional method.

THE PROCEDURE EVERYTHING IS THE SAME, BUT DONE ON A MINIATURE SCALE, THAT'S ALL.

Semi micro filtration arrangement

Over a water - trough having a diameter of about 2 feet a 1/4 HP water - suction motor is mounted. The outlet of the motor is connected to one end of a water - suction filter tube mounted inside the trough. The other end of this tube is connected to a semimicro filter tube outside the trough. This way the filtration will be fast, effective and the water will be recirculated into the water trough itself.

Separation of Organic mixtures

This can be done with the help of pasteur pipette

with a rubber head. The open end of it is plugged with cotton, to avoid the entry of solids. The advantages are we can,

i) remove traces of solvent lying over the solid substances.

ii) separate the lower / upper layers of two immisicible liquids as desired.

iii) less amount of ether is sufficient to carry out mixture separations.

iv) Upon crystallisation the supernatant liquid can be easily transferred.

Determination of Physical constants

With regard to m.pt. we do it in the capillary tube, so no problem about the quantity of the substance to be used. B.pt. can be done with the help of a capillary tube. The liquid for which b.pt. is to be determined is taken in one capillary tube. Another capillary tube is elongated by showing in the flame. The elongated side can be inserted into the first one, Of course the unelongated side is fused before insertion. The temperature at which rise of liquid in the inserted tube takes place is the b.pt.

Reactions on Porcelain Tile

Solubilities of substances can be done on porcelain tile instead of in capillary tubes. Similarly reactions can also be done on tiles instead of in capillary tubes. Thus the capillary reactions have given way to the tile reactions. The solubilities can throw some light on the functional nature of the substances as to acid, phenol, amine or neutral. The observations and inferences are the same similar to the conventional method. But, to save time for the learners they are once again given here.

ANALYSIS OF AN ORGANIC COMPOUND

Experiment	Observation	Inference

1. Test For Aromaticity:

Substance is introduced into the flame using a nickel spatula.	**i. Burns with a smoky flame**	**Presence of aromatic compound**
	ii. Burns with a non - smoky flame	**Presence of aliphatic compound**

Theory:

The percentage of hydrogen is less in aromatic compounds than in aliphatic compounds. So the amount of heat liberated by the oxidation of hydrogens of aromatic compounds is less. As a result the carbons in aromatic compounds are incompletely oxidised. This leads to a sooty flame.

b. Substance is added to a mixture of 3 drops of con.sulphuric acid & 3 drops of con. nitric acid and warmed on a water bath for about 10 minutes. The solution is poured, then into water.	**An yellow solution or precipitate is obtained.**	**Presence of aromatic compound**

Theory:

The yellow colour is due to the formation of nitro compounds by the nitration of aromatic compounds.

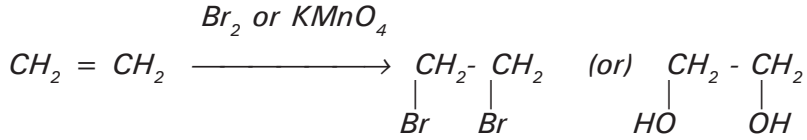
2. Test For Unsaturation

(a)	A little of the substance or a drop of the substance as the case may be is taken on a tile. A drop of concen--trated bromine water is added to it.	(i) Decolourisation	Presence of Unsaturation
		(ii) Decolourisation followed by turbidity formation	Presence of aniline (or) phenol (or)

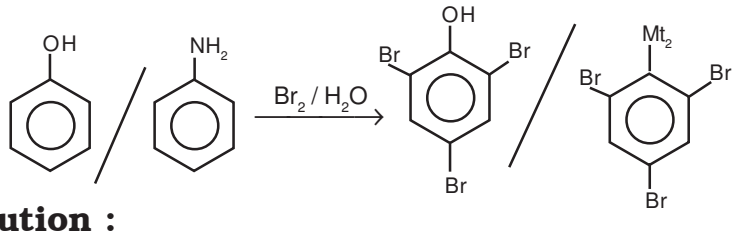
b) A pinch of the substance is taken on a tile. A drop of dil pottassium permanganate is added to it.	Decolouration	Presence of unsaturation (or) easily oxidisable compound

Theory:

Unsaturated compounds form dibromides and diols respectively with bromine and potassium permanganate.



Phenols and aniline form their respective s- tribromo compounds, by substitution of the aromatic nucleus, which are white.



Caution :

Phenols and aniline also decolourise potassium permanganate. This is because they are susceptible to oxidation by permanganate.

SODIUM FUSION EXTRACT TESTS : (LASSIAGNE'S TEST)

Two small cut pieces of sodium are fused in a semimicro hard glass tube. About 5mg of the substance is added to it and fused again. The tube is cooled to room

temperature. Keeping the tube in a slanting position 4 drops of water are added.(the first drop of water is allowed to react with excess of sodium. The second dop is added after the initial reaction is over. Then the third and the fourth drops of water are added slowly). This is the sodium fusion extract. The following tests are performed with it.

THEORY:

The organic compound containing C, H, O, N, S and Hal, on fusion with sodium will be converted into sodium cyanide, sodium sulphide, sodium halide and sodium hydroxide. Excess of sodium is essential to perform this test. The reason is N& S,if both present , sodium thiocyanate, NaCNS, may be formed. This will interfere with the prussian blue colour nitrogen. When excess of sodium is used this will be decomposed.

$$NaCNS + 2Na \longrightarrow NaCN + Na_2S$$

TEST FOR NITROGEN:

A drop of the extract is placed on a tile. A drop of a concentrated solution of ferrous sulphate is added to it. Then it is treated with a drop of 50% Sulphuric acid.	Prussian blue colour	Presence of Nitrogen

THEORY :

The extract on treating with ferrous sulphae solution forms sodium ferrocyanide.Upon treatment with con. Sulphuric acid the ferrous and ferric hydroxides (formed by the air oxidation of ferrous ion) get dissolved. The ferrocyanides react with the Fe^{3+} ions producing ferric ferrocyanide (Prussian Blue).

$$FeSO_4 + 6\ NaCN \longrightarrow Na_4[Fe(CN)_6] + Na_2SO_4$$
$$3\ Na_4[Fe(CN)_6] + 2\ Fe_2(SO_4)_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 6\ Na_2SO_4$$

TEST FOR HALOGENS:

A drop of the extract is placed on a tile. A drop of con.Nitric acid is added followed by a drop of silver nitrate solution.	i. Curdy white precipitate	Presence of chlorine
	ii. Pale yellow precipitate	Presence of bromine
	iii.Yellow precipitate	Presence of iodine

THEORY:

i.The extract is treated with con.Nitric acid, before the precipitation of the silver halides. This is to ensure the removal of hydrocyanic acid and hydrogen sulphide from the reaction medium.

ii. The halogens are precipitated as their silver halides.

$$NaX + AgNO_3 \longrightarrow AgX + NaNO_3$$

iii. Silver chloride forms an argentamine complex with ammonium hydroxide, which is soluble in excess ofammonium hydroxide. Because of their larger size, the silver halides of bromine and iodine are either sparingly soluble or insoluble in ammonium hydroxide.

If halogen is present,

About 5 mg of the substance is warmed with 3 drops of alcoholic silver nitrate on a water bath and acidified with a drop of con.con.Nitric acid.	i. Immediate formation of a precipitate	Halogen is present in the side chain
	ii. No precipitate	Halogen is present in the aromatic nucleus

THEORY:

In the former the halogen is somewhat ionic, hence comes out readily as silver halide. When the halogen is attached to the nucleus it will not come out readily.

Test for Sulphur:

iii)	A drop of the extract is mixed with a drop of sodium nitroprusside on a tile.	Violet Colouration	Presence of sulphur

Theory :

Sodium sulphide, in the extract reacts with nitroprusside to give an addition complex, which is violet in colour.

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$$

Sodium nitroprusside

iv)	A drop of the extract is tested with a drop of lead acetate solution on a tile.	Black precipitate	Presence of sulphur

Theory :

Sulphur gets precipitated as follows :

$$Na_2S + Pb(OAC)_2 \rightarrow pbS + 2\ NaOAC$$

5. Solubility Tests:

Solubility of the substance in the following solvents are tested.

i. Water	**Soluble**	**Presence of urea carbohydrates etc.,**
ii. 5% Sodium bicarbonate	**Soluble**	**Presence of acids**
iii. 5% Sodium hydroxide	**Soluble**	**Presence of acids, phenols**
iv. 5% Hydrochloric acid	**Soluble**	**Presence of amines**

6. Action on Litmus :

Moistened litmus paper is brought into	**i. Blue litmus turns red**	**May be due to acids, phenols.**

contact with the substance.	**ii. Red litmus turns blue**	**May be due to amines**
	iii. Neutral	**Presence of carbohydrates esters, carbonyls etc.**

7. Action of Sulphuric Acid :

About 5 mg of the substance is warmed with 3 drops of con. sulphuric acid.	**Substance chars with the smell of burnt sugars**	**Presence of carbohydrates**

Theory :

Carbohydrates are dehydrated completely by sulphuric acid leaving a charred carbon mass.

$$Cn(H_2O)\,n \xrightarrow{Con.\ H_2SO_4} nC + nH_2O.$$

8. Test for carboxylic acid :

a)	About 5 mg of the substance is treated with a drop of highly saturated sodium bicarbonate solution on a tile.	Brisk effervescence	Presence of carboxylic acid

Theory :

Carboxylic acids react with bicarbonate to liberate carbon di oxide according to the equation.

$$RCOOH + NaHCO_3 \rightarrow RCOONa + H_2O + CO_2 \uparrow$$

b)	A drop of neutral ferric chloride solution is added to a little of the substance	i)Violet colour	Presence of salicylic acid
		ii)Flesh colour	Acids like phthalic,

Theory:

As under phenols.

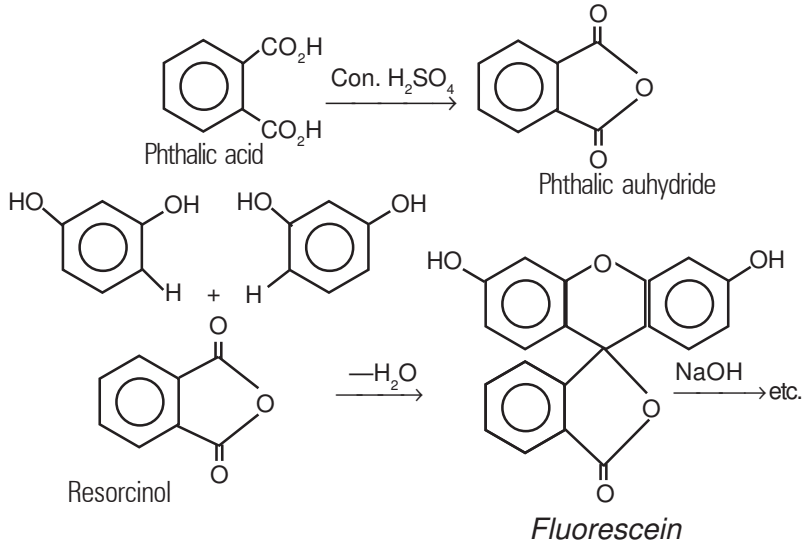
9. Test for ortho - dicarboxylic acid :

About 5 mg of the substance is heated with an equal amount of resorcinol and 1 drop of con. sulphuric acid in a semimicro tube.		
This mixture taken on the tip of a glass rod is slowly immersed into a Semi Micro test tube containing about 2.5 ml of water and 3 drops of 50% Sodium hydroxide	Green fluorescence	Presence of ortho dicarboxylic acid

Theory:

The formation of the green fluorescence may be explained as follows: The dicarboxylic acid (those on adjacent carbon atoms) undergoes dehydration to give the cyclic anhydride. This then combines with two molecules of resorcinol to give fluorescein, which is red in colour. When dil. alkali is added to the above solution, the fluorescein gives an intense green fluorescence. The lactone ring is cleaved simultaneously to produce an anion comparable in structure to the anion produced from phenolphthalein.

Example



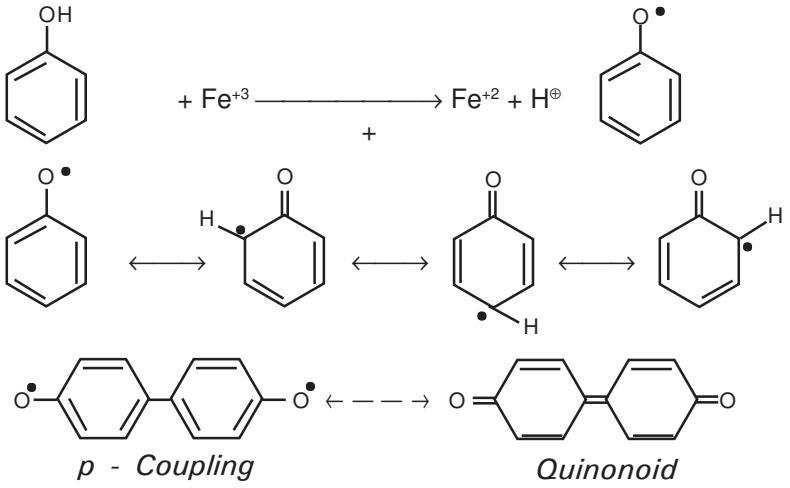
10. Test for Phenol:

Neutral Ferric chloride test :

A drop of the substance is mixed with a drop of neutral ferric chloride solution on a tile.	Violet colouration	Presence of phenol

Theory of ferric chloride oxidation :

When ferric chloride is added to a phenol, oxidation of the hydrogen of the hydroxyl group of phenol takes place. This is due to the presence of 'one-electron transfer' oxidising agent, Fe^{+3} ions. The first step of the reaction is the formation of the phenoxy radicals, which are highly coloured. In the second step, these phenoxy radicals undergo coupling reaction.

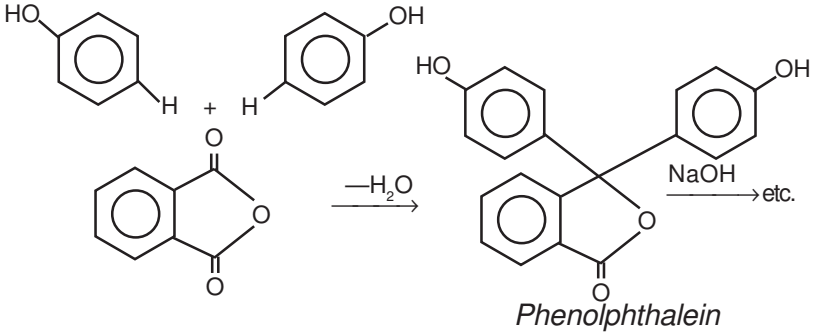


Phthalein Reaction:

About 5 mg of the Substance is heated with about 10 mg of phthalic anhydride and a drop of con. sulphuric acid in a sermimicro tube. The solution is cooled and diluted with about 1 ml of water. A drop of the solution is mixed with a drop of 50%, sodium hydroxide solution on a tile.	Red, blue or green colour is produced	Presence of phenols

Theory:

Phenols react with phthalic anhydride to form ***phthaleins.*** *Hence the name phthalein reaction.*



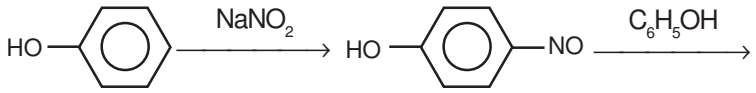
When this is made alkaline we get an anion, which is red in colour. This is due to the opening of the lactone ring as well as the formation of a quinonoid ring system.

Liebermann's reaction :

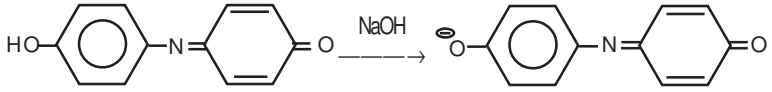
About 5 mg of the substance is heated with about 5 mg of sodium nitrite and 2 drops of con. sulphuric acid in a semi micro tube. It is cooled and diluted with about 1 ml of water. A drop of it is placed on a tile and mixed with a drop of 10% sodium hydroxide solution.	A bluish green colour is produced	Presence of Phenols

Theory:

Nitrous acid formed by the reaction of sodium nitrite and sulphuric acid attacks the phenol at the para position. The p-nitrosophenol then combines with another molecule of phenol to give INDOPHENOL (Red). This on basification gives indophenol anion which is blue in colour. Polyhydric phenols give bluish green colour.



Phenol *p - Nitrosophenol*



Indophenol (Red) *Indophenol Anion (Bluish Green)*

Test for α-Naphthol (Molisch's test)

A drop of the alcoholic solution of the substance is placed on a tile. It is mixed with a drop of an aqueous solution of glucose. To this a drop of con. sulphuric acid is added.	Violet colouration	Presence of α - naphthol

Theory:

The furfural derivatives formed by the action of sulphuric acid produce a violet colouration at the junction of the two liquids, either in the cold or on warming gently. The colour is believed to be due to the formation of a triphenylmethane - type dye between α-naphthol and a furfural.

Test for β-Naphthol

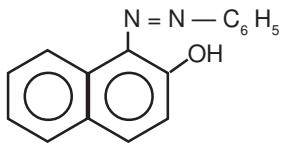
A drop of aniline is placed on a tile. A drop of dil. hydrocholoric / sulphuric acid is added to it. A drop of saturated sodium nitrite solution is added. Then a drop of alkaline solution of the substance is added to it.	A scarlet red dye	Presence of β - naphthol

Theory:

The aniline is diazotised initially by the action of nitrous acid produced by the reaction of sodium nitrite and hydrochloric acid. Upon coupling with an alkaline solution of the substance it gives the red azo dye. This reaction is characteristic of β - naphthol.

$$PhNH_2 \xrightarrow{NaNO_2 \,/\, HCl} PhN_2^+ Cl^-$$

$$Ph\,N_2^+ Cl^- \xrightarrow[\beta\text{ - Naphthol}]{\text{Alkaline}}$$



1 - phenylazo - 2 - naphthol

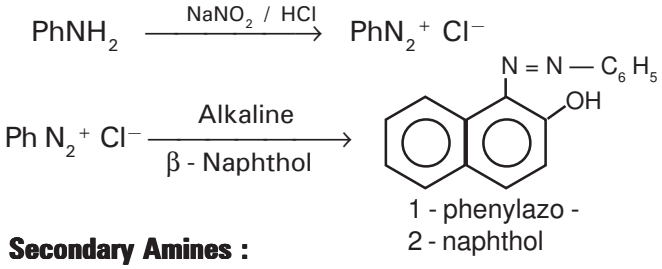
Test for primary Amines :

Dye test :

A drop of the substance is placed on a tile. A drop of dil. hydrochloric acid is added to it. A drop of saturated sodium nitrite solution followed by a drop of β -naphthol dissolved in 25% sodium hydroxide is added to it.	Red azo dye	presence of aromatic primary amine

Theory:

The aniline is diazotised initially by the action of nitrous acid produced by the reaction of sodium nitrite and hydrochloric acid. Upon coupling with an alkaline solution of the substance it gives the red azo dye. This reaction is characteristic of β - naphthol.



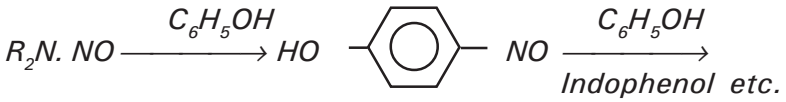
1 - phenylazo - 2 - naphthol

Test for Secondary Amines :

2 drops of substance, 2 drops of dil. hydrochloric acid and 2 drops of saturated solution of sodium nitrite are taken in a semimicro tube. A drop of con. sulphuric acid and a drop of phenol are added. Heated for a minute. A drop of this solution is mixed with a drop of dil sodium hydroxide on a tile.	A bluish green colour is produced	presence of secondary amine.

Theory:

The nitrous acid formed by the action of sulphuric acid on the nitrosoamine gives p- nitrosophenol on reaction with phenol. This on further reaction gives indophenol (red). The latter on basification with sodium hydroxide forms indophenol anion, which is blue in colour.

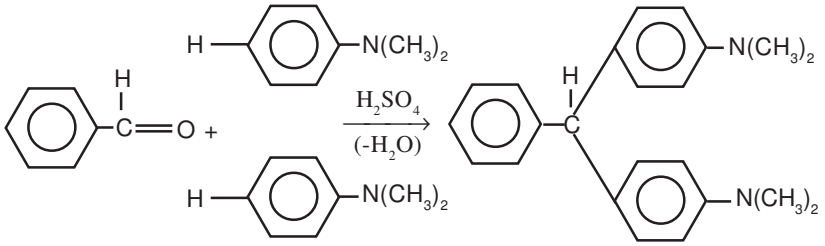


Dye test:

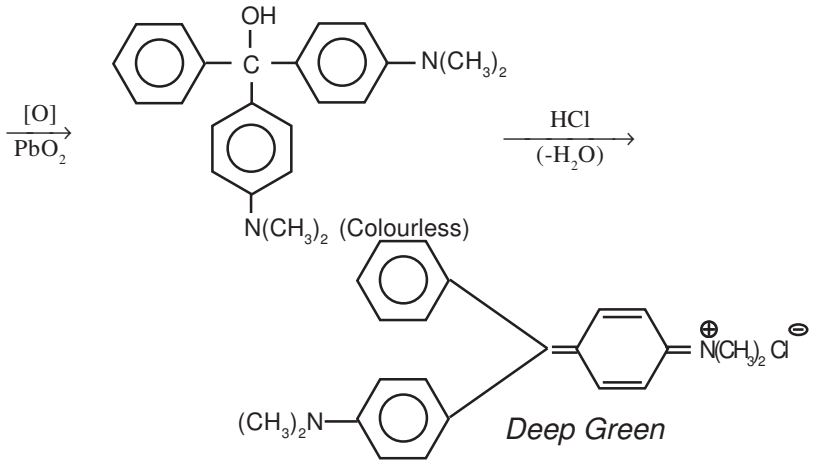
2 drops of benzaldehyde and 4 drops of the substance are heated with 1 drop of con. sulphuric acid, then it is heated with about 50 mg of lead di oxide. A drop of this solution is mixed with a drop of dil. Hydrochloric acid on a tile.	Deep Green dye is obtained	presence of tertiary amine.

Theory

Benzaldehyde reacts with tertiary amine in the presence of sulphuric acid to give LEUCO BASE. This upon oxidation with lead dioxide and treatment with hydrochloric acid gives the malachite green dye.



Benzaldehyde *N, N - Dimethylaniline* *Leuco Base*



Test for nitro group :

a) Reduction to amines :

About 3 drops of the substance is reduced with 3 drops of con. hydrochloric acid and metallic tin or zinc in a semimicro tube, by heating for about 5 minutes. with a drop of the supernatant liquid dye test is performed on a tile. (as under test for amines)	Red azo dye	Presence of nitro compound

Theory

$$R - NO_2 \xrightarrow{Zn \ \& \ HCl} RNH_2$$

$$R - NH_2 \xrightarrow{NaNO_2 / HCl} RN_2^+ Cl^-$$

(Rest as under test for β - naphthol)

Test for Mulliken - Barker's test :

About 3 drops of the substance and 3 drops of alcohol are boiled with 3 drops of calcium chloride solution and a pinch of zinc dust. Heated to boiling and cooled. A drop of it is mixed with a drop of Tollen's reagent on a tile.	A black precipitate is formed	Presence of nitro compound

Theory:

The nitro compound is reduced to hydroxylamine by zinc & calcium chloride. The hydroxylamine compound on reaction with Tollen's reagent gives silver hydroxide which readily decomposes to give the black silver oxide.

Test for Anilide :

About 10 mg of the substance is heated strongly in a dry semi micro tube with sodalime. The resulting vapour is collected in another semi	Scarlet Red dye	Presence of

micro tube containing 5 drops of dil. hydrochloric acid. With a drop of the acid solution dye test is performed.		anilide

Theory:

The anilides give out aniline vapours when heated with sodalime. Thereafter it is similar to the dye test carried over on the primary amine.

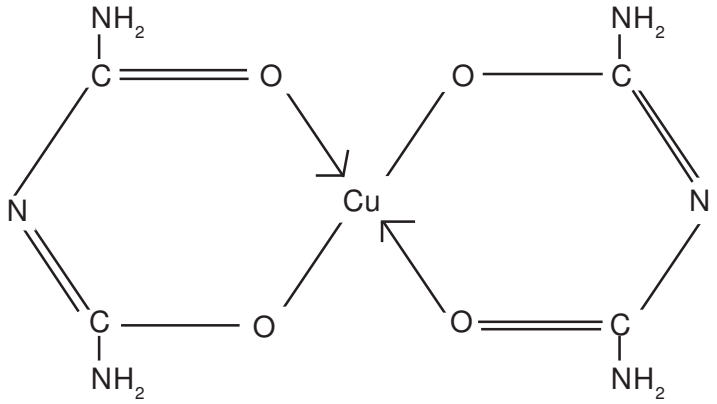
Biuret test :

About 5 mg of the substance is heated strongly in a DRY semi micro tube to its melting point. Cooled, dissolved the residue in 3 drops of water. A drop of it is mixed with a drop of dil. copper sulphate and a drop of dil. sodium hydroxide solutions on a tile.	A violet colouration is produced	Presence of diamide.

Theory:

The urea on heating to its m.pt. forms hydrocyanic acid. This combines with a second molecule of urea to form the Biuret. The Biuret forms a chelate complex with the cupric ion giving the violet colouration.

$$Urea \xrightarrow{\Delta} H_2N - CO - NH - CO - NH_2 \text{ (Biuret)}$$

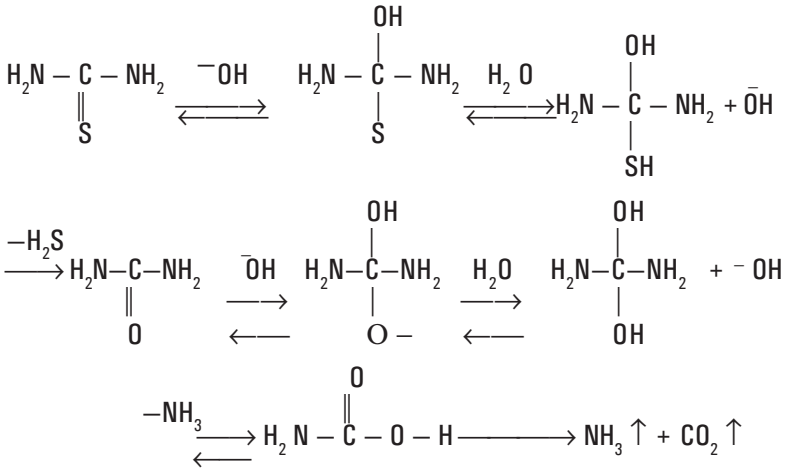


Test for thiourea :

a)	About 5 mg of the substance is heated with 5 drops of dil. sodium hydroxide solution, cooled. A drop of it is mixed with a drop of lead acetate solution on a tile.	A black or brown precipitate	Presence of thiourea.

Theory:

Thiourea may be decomposed by sodium hydroxide into hydrogen sulphide, ammonia and carbamic acid as follows.



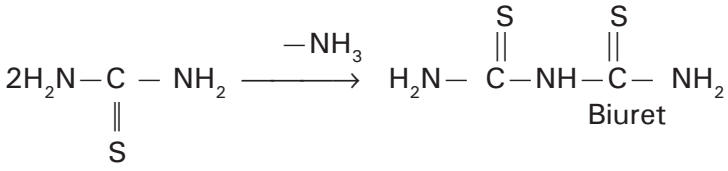
The hydrogen sulphide in solution may then react with lead acetate to form lead sulphide, which is obtained as a black precipitate.

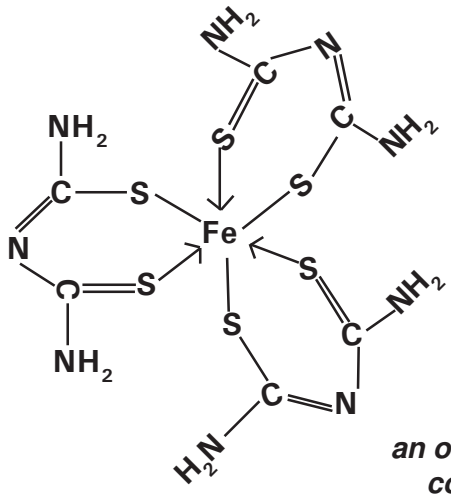
$$H_2S + Pb(OAc)_2 \longrightarrow PbS \downarrow + 2\ HOAc$$

b)	5 gm of the substance is heated in a Dry semi micro tube until it melts. Cooled and then dissolved the residue in 4 drops of water. A drop of this solution is mixed with a drop of neutral ferric chloride solution on a tile.	Blood red colouration	Presence of thiourea

Theory :

On heating, thiourea forms a Biuret derivative. This forms an octahedral complex with iron as the central metal atom.





an octahedral complex

Test for Aromatic monoamide:

a)	About 5 mg of the substance is heated with 5 drops of 25% sodium hydroxide solution, cooled. A drop of it is mixed with a drop of con. hydrochloric acid.	White ppt.	presence of monoamide.

Theory:

Amides on hydrolysis with alkali give the corresponding sodium salt of the acid. This upon acidification generates the free acid.

On heating the amide with sodium hydroxide, the sodium salt of the acid and ammonia are formed. The latter escapes from the reaction mixture during heating. This can be tested by showing a glass rod dipped in con.hydrochloric acid at the mouth of the test tube. Dense white fumes of ammonium chloride will be formed.

On acidification, the acid separates as a white solid. Of course the reaction mixture should be cooled to get maximum amount of the acid.

$$RCONH_2 + NaOH \longrightarrow RCOONa + NH_3 \uparrow$$

$$RCOONa + HCl \longrightarrow RCOOH + NaCl$$

Test for Carbohydrates:
(Molisch's test)

A drop of an alcoholic solution of α - naphthol is mixed with a drop of the aqueous solution of the substance on a tile. This mixed solution is allowed to come in contact with a drop of con. sulphuric acid	A deep violet colouration	Presence of sugars

Theory:

as under α - naphthol

Test for aldehydes / ketones:
Borsche's reagent test:

A drop of the substance (if it is a liquid) or a drop of an alcoholic solution of the substance is placed on a tile. A drop of a concentrated solution of 2, 4 - DNP (Borsche's reagent) is added to it.	Red orange ppt	Presence of aldehyde / ketone

Theory:

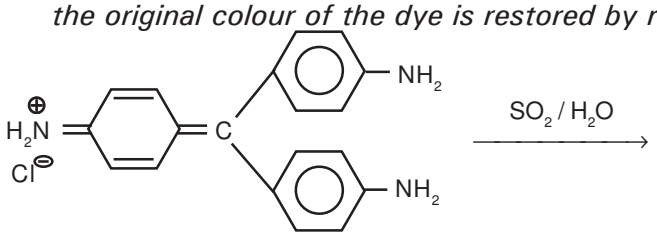
The phenylhydrazine reacts with the carbonyl compunds to form their corresponding 2.4-dinitrophenylhydrazones.

Schiff's reagent test :

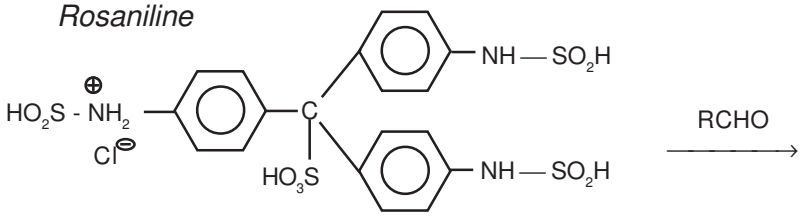
A drop of the substance is placed on a tile. A drop of Schiff's reagent is mixed with it.	Pink colouration	Presence of aldehyde

Theory:

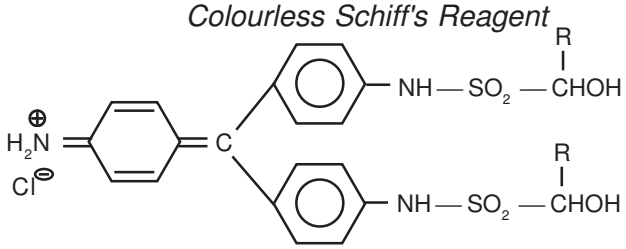
schiff's reagent is a very, very dilute solution of p-rosaniline hydrochloride in water, decolourised using sulphur dioxide. Upon shaking with aldehydes the original colour of the dye is restored by reoxidation.



Rosaniline



Colourless Schiff's Reagent



Aldehyde Addition Product (Coloured)

Fehling's Test:

2 drops or about 5mg of the substance is mixed with 2 drops of Fehling A and 2 drops of Fehling B solutions in a Semimino test tube. It is heated in a water bath for about 5 minutes.	Red precipitate	Presence of aldehydes / reducing sugars.

Theory:

Fehling A solution is nothing but copper sulphate dissolved in water. Fehling B is an alkaline solution of sodium potassium tartrate or otherwise called as Rochelle salt. When both Fehling A and Fehling B solutions are mixed blue cupric hydroxide gets prescipitated. This will be reduced to cuprous oxide by the aldehydes, thereby getting themselves oxidised to carboxylic acids.

$$RCHO + 2Cu(Tart)_2^{2-} + 5\,\bar{O}H \longrightarrow Cu_2O\downarrow + RCOO^- + 4\,Tart^{2-} + 3H_2O$$

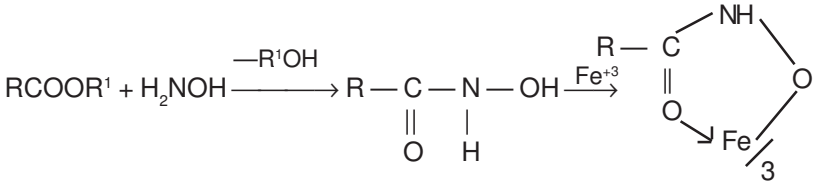
$$Tart = \begin{array}{l} CHOH - COO^{\ominus} \\ | \\ CHOH - COO^{\ominus} \end{array}$$

Test for ester :

a)	About 2 drops of the substance is heated with 2 drops of methanolic solution of hydroxylamine hydrochloride and 2 drops of 50% sodium hydroxide & cooled, A drop of it is placed on a tile. A drop of dil. hydrochloric acid is added to it.Then a drop of neutral ferric chloride is added to it.	Violet colour	Presence of ester

Theory:

Ester reacts with hydroxylamine to give hydroxamic acid. This gives a deep violet colouration with aqueous Fe^{+3} ion, owing to the formation of a chelate complex.



Chelate Complex

b)	2 drops of the substance is heated with 2 drops of 50% sodium hydroxide solution, till it is dissolved, cooled and then added 4 drops of 50% hydrochloric acid.	White precipitate	Presence of ester

Theory:

The ester undergoes simple alkaline hydrolysis to form the sodium salt of the acid. To liberate the free acid we have to acidify the solution.

$$RCOOEt + NaOH \longrightarrow RCOONa + EtOH$$

$$RCOONa + HCl \longrightarrow RCOOH + HCl$$

Caution:

Amides also will give solid acids for this test. But can be distinguished from the esters by their liberation of ammonia. When a glass rod dipped in con. hydrochloric acid is shown at the top of the condenser, dense white fumes will be observed.

DERIVATIVE PREPARATION

(Depending on the availability of chemicals, the quantities may be proportionately reduced)

Having made the identification of a compound as to belong to a particular class of compounds, it is necessary to confirm it by preparing a suitable derivative. The following points may help one towards the preparation of a satisfactory derivative.

i) The derivative should preferably be prepared easily in good yield by an unambiguous reaction. It is better to prepare solid derivatives than liquids, since the former is easy to handle.

ii) It is again preferable to use a general reaction for derivatisation.

iii) The properties of the derivatives should be distinctly different from the parent compound.

The methods of preparation of derivatives for certain classes of compounds are given under.

For Aldehydes and Ketones : (1-4)

1) 2, 4 - Dinitrophenylhydrazone :

About 0.2g of the substance is dissolved in alcohol. To this about 2 ml of Borsche's reagent and a few drops of con. hydrochloric acid are added. Heated to boiling and allowed to cool. The precipitate is filtered and recrystallised from alcohol.

2) Phenyl Hydrazone :

1 gm of phenylhydrazine hydrochloride and 1.5 gm of and sodium acetate are dissolved in minimum amount of water. The solution is then added to 0.5 gm of the substance in alcohol. The mixture is shaken well until a clear solution is obtained. Then warmed for about 15 minutes on a water bath and cooled. The precipitate is filtered and recrystallised from dil. alcohol.

3) Oxime :

0.5g of hydroxylamine hydrochloride is dissolved in 2 ml of water. 2 ml of 10% sodium hydroxide solution and 0.2g of the substance are added to it. (If the solution is not clear, then little alcohol may be added to make it clear).

The mixutre is heated under reflux for about 15 minutes and then cooled in ice (If no precipitate separates on cooling, then it may be diluted with 2-3 volumes of water)

4. Semicarbazone :

1 gm of semicarbazide hydrochloride (H_2N-CO-NH-NH_2.HCl) and 1.5 gm of sodium acetate are dissolved in minimum amount of water. To this is added a solution of 0.5 gm of the substance in alcohol. The mixture is then shaken well and heated on a water bath for 15 minutes and cooled. The precipitate is filtered and recrystallised from alcohol.

For Amides :

For ALIPHATIC diamides : (5,6)

5. Nitrate Derivative :

To a saturated solution of the amide in water, con. nitric acid is added drop by drop till a precipitate is formed. The crystals are filtered and recrystallised from dil. alcohol.

6. Oxalate Derivative : ($2\ CO(NH_2)_2 . H_2C_2O_4$)

To a saturated solution of the substance, a saturated solution of oxalic acid is added slowly till a precipitate is formed. It is recrystallised from dil. alcohol.

For AROMATIC Amides.

7. Acid Derivative

1 gm of the substance is hydrolysed by heating with 10 ml of 10% sodium hydroxide and the acid is

isolated after acidification with dil. hydrochloric acid. It is recrystallised from hot water.

For Amines : (8, 9, 10)

8. Benzoyl Derivative (Schotten - Baumann Reaction):

The amine is treated with a little excess of sodium hydroxide (5 ml) in a boiling tube, 1 ml of benzoyl chloride is added in small amounts with constant shaking. The boiling tube is tightly corked and shaken well for 5-10 minutes. The solid is filtered and washed well with water to remove the excess alkali. It is recrystallised from alcohol.

Theory:

When the primary amine is treated with sodium hydroxide, the acidic hydrogen is removed. As a result, RNH^- ion is produced. This acts as a nucleophile and help displace the chlorine atom from benzoyl chloride. Thus facilitating the formation of the benzoate ester. The hydrochloric acid liberated will be neutralised by the sodium hydroxide present in the reaction medium.

9. Bromo Derivative:

1 gm of the substance is dissolved in 1 ml of glacial acetic acid. To this is added bromine in glacial acetic acid till the colour of the bromine persists. After 15 minutes the mixture is poured into cold water. It is filtered and recrystallised from alcohol.

Theory :

As under TEST FOR UNSATURATION

10. Acetyl Derivative :

0.5 gm of the amine is refluxed with 2-3 ml of acetic anhydride and 0.5g of powdered sodium acetate in a DRY boiling tube for 10-15 minutes, using an air condenser. The reaction mixture is cooled and poured into 20 ml of water. The solution is boiled to decompose the

excess acetic anhydride,cooled and filtered. It is recrystallised from alcohol.

Theory :

The amine is acetylated to form anilides

$RNH_2 + AC_2O \longrightarrow RNHAC + HOAC$

For Secondary Amines :

Benzoyl and acetyl derivatives may be prepared using the same procedure as under PRIMARY AMINES.

11. Picrate :

See test for HYDROCARBONS.

For TERTIARY AMINES :

12. Picrate :

See test for HYDROCARBONS.

For ANILIDES : (13 & 14)

13. Bromo Derivative :

Proceed as under PRIMARY AMINES.

14. Nitro Derivative:

0.5 gm of the substance is dissolved in a mixture of 3 ml of con. sulphuric acid and 3 ml of con. nitric acid. The mixture is warmed for 5 minutes, cooled and then poured into ice water.

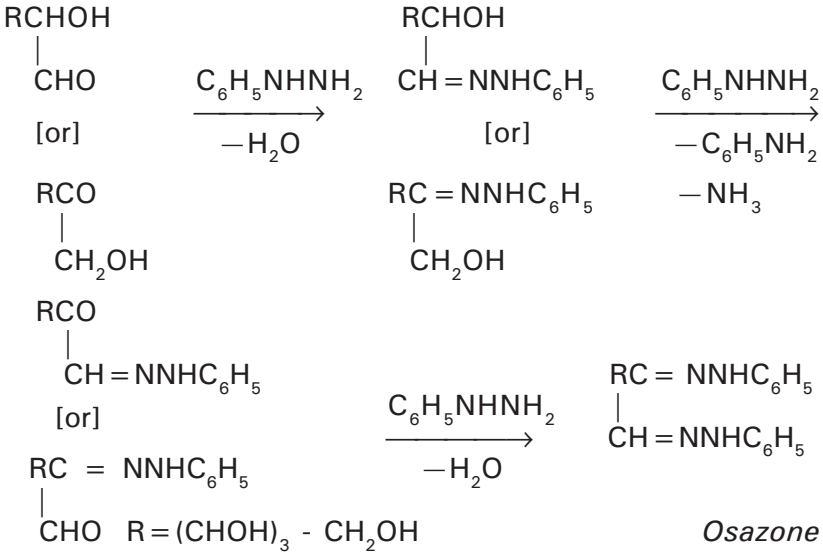
FOR CARBOHYDRATES :

15. Osazone Derivative:

To 5 ml of a 1% solution of the compound, a mixture of 0.1g of phenylhydrazine hydrochloride and 0.25g of sodium acetate are added. Then 3 drops of glacial acetic acid are also added. The mixture is heated on a boiling water bath for 15 minutes. The osazone is recrystallised from dil. alcohol.

Theory:

Initially one molecule of phenylhydrazine reacts with the sugar to give the respective phenylhydrazone. Then the carbon neighbour to the hydrazone is oxidised to a carbonyl group. This then combines with another molecule of phenylhydrazine to give the osazone.



For CARBOXYLIC ACID: (16 & 17)

16. Amide Derivative :

0.5 g of the substance is mixed with twice its weight of phosphorous pentachloride in a DRY boiling tube with the help of a glass rod. The mixture is gently warmed for a minute. It is cooled and a few ml of liquor ammonia are added drop by drop, carefully. The amide is then recrystallised from hot water.

Caution:

The reaction is highly Exothermic.

17. S- Benzylisothiuronium Chloride Derivative:

0.5g of the substance is suspended in 10 ml of hot water. A drop of phenolphthalein is added and then

neutralised carefully with dil. sodium hydroxide solution. Then 2 drops of dil. hydrochloric acid are added to make it faintly acidic. This is added to a saturated solution of S-Benzylisothiuronium chloride. The mixture is then cooled till precipitation is completed. It is recrystallised from dil. alcohol acidifed with dil. hydrochloric acid (This derivative is suitable for sulphonic acids also).

For ESTERS :

18. Acid Derivative:

See test for ESTERS.

For HYDROCARBONS:

19. Picrate Derivative :

Proceed as under test for HYDROCARBONS:

20. Nitro Derivative :

a. For HYDROCARBONS:

0.5g of the substance is added to 2 ml of con. sulphuric acid. Then 2 ml of con. nitric acid is added drop by drop. The whole mixture is heated for 5 minutes, cooled and then poured into 20 ml of water. It is filtered and recrystallised from hot alcohol.

b. For PHENOLIC ACIDS :

0.5 gm of the substance is boiled with 2 ml of dil. nitric acid and then diluted with water. The nitro derivative is recrystallised from hot alcohol.

21. For NITRO COMPOUNDS :

Further Nitration: (polynitro derivative)

About 0.5 gm of the substance is first dissolved in 1 ml of con. sulphuric acid. To this is added 2 ml of nitrating mixture (I ml of con. sulphuric acid + 1ml of con. nitric acid). Boiled for about 15 minutes with an air condenser. The heating is stopped when a test portion of the reaction mixture gives a solid with cold water. The

entire mixture is then poured into water and stirred well. The solid is collected by filtration.

For PHENOLS: (22 & 23)

22. Bromo Derivative:

To about 0.5 ml of phenol, bromine water is added slowly with constant stirring until a pale yellow colour persists. The precipitated tribromophenol is filtered and crystallised from dil. alcohol.

23. Benzoyl Derivative:

Proceed as under AMINES.

Inorganic Qualitative Analysis

1. Test for Carbonate

About 3 mg of the salt is taken on a porcelain tile and added a drop of dil.H_2SO_4/dil.HCl .	Brisk Effervescence is noted	Presence of carbonates is confirmed

2. Test for Nitrate

To about 3 to 5mg of salt in a semimicro tube , 3 drops of conc.H_2SO_4 and a small filter paper rolled into a ball is added and heated.	Reddish brown fumes	Presence of Nitrate is confirmed

3. Test for Halides

To about 3 – 5 mg of salt in a semimicro tube 3 drops of Con.H_2SO_4 are added and heated.	i.Colourless gas giving dense white fumes with a glass rod dipped in dil.NH_4OH	Presence of Chloride
	ii.Reddish brown fumes	Presence of Bromide
	iii.Violet vapours	Presence of Iodide
	iv. Oily drops on the sides of the tube.	Presence of Fluoride

4. Test for Phosphate

3-5mg of the salt in a semi-micro test tube is heated with 3 drops of , Con. HNO_3 .The hot solution is added to 3 drops ofAmmonium Molybdate taken in another test tube.	(i) Canary Yellow ppt. in the cold	PresenceofPhosphate

4. Test for Oxalate

3-5mg of the salt is heated with 3 drops of dil.H_2SO_4, To the hot solution a pinch of MnO_2 is added.	Brisk effervescence	Presence of oxalate

Test for Borate

3-5 mg of the salt is heated with 2 drops of alcohol and one drop of con. H_2SO_4. The evolving vapours are ignited.	Green edged flame	Presence of Borate

For Basic Radical Analysis

Instead of doing elimination of interfering radicals, the residue obtained in sodium carbonate extract prepration can be used for Basic Radical analysis.

INORGANIC QUANTITATIVE ANALYSIS

1. Modified Procedure for Volumetric Experiments: (Use of Microscale Technique)

The scaling down of quantities can also be extended to other experiments like volumetric

At present, estimation is done by using a pipette, a burette and conical flask. It has been realized now that taking solution by a pipette may prove to be dangerous. Sometimes the solution sucked by a pipette may be corrosive or toxic or may be strong enough to damage parts of the mouth. Hence it is recommended that use of a pipette for titration should be abandoned wherever possible. Instead a burette may be used to take a fixed volume of the solution. This method is called a two burette method. Where high accuracy of titration reading is expected, this method can be used by using a micro burette.

Two Burette Method

Let us consider a simple titration between oxalic acid solution (approx. 0.05 N) and NaOH solution (0.05 N) using phenolphthalein indicator. Let us take Oxalic acid solution as a titre (a solution with unknown concentration) in burette 1 and NaOH solution as a titrant (a solution with known concentration) in burette 2. Let us say that we take 10 ml of 0.05 N Oxalic acid by burette 1 in a conical flask. We add to it 3 to 4 drops phenolphthalein indicator. Since the medium is acidic, the solution remains colourless. Now we add NaOH solution drop by drop by from burette 2. At some stage the indicator changes its colour i.e. the solution becomes pink. We note this burette reading B1. To the pink solution in the conical flask, now we add one ml Oxalic acid solution from burette 1. Since the solution in the conical flask becomes acidic, the indicator changes its colour and the solution becomes colourless. To the same solution, without adding any indicator, we add in a dropwise manner NaOH solution by burette 2. At some stage, the indicator changes its colour i.e. the solution becomes pink. We note this burette reading B 2. To the pink solution in the conical flask, we add

one ml Oxalic acid solution from burette 1. Since the solution in the conical flask is acidic, the indicator changes its colour and the solution becomes colourless. To this solution, without adding any indicator, we add in a dropwise manner NaOH solution by burette 2. At some stage, the indicator changes its colour i.e. the solution becomes pink. We note this burette reading B3. In this manner, every time we add one ml Oxalic acid so that the solution becomes colourless and then add NaOH solution in a drop wise manner till the solution becomes pink. We take at least five burette readings B 1 to B5. Thus the titration can get over by using 14 ml Oxalic acid and about 15 ml NaOH as against the volume of 30 to 40 ml Oxalic acid and NaOH, required by the conventional method.

Observation Table :

Titration between 10 ml Oxalic acid (approx. 0.05 N) and NaOH (exact 0.05N).

Titre: Oxalic acid Titrant: NaOH

Indicator: Phenolphathalein End Point: Colourless to pink.

Table: Titration of Oxaic acid Vs NaOH

Titre	Titrant
10 ml	B_1
11 ml	B_2
12 ml	B_3
13 ml	B_4
14 ml	B_5

Calculation : N_1V_1

	Oxalic acid				**NaOH**		
1)	N_1	x	10	=	0.05	x	B_1
2)	N_2	x	11	=	0.05	x	B_2
3)	N_3	x	12	=	0.05	x	B_3
4)	N_4	x	13	=	0.05	x	B_4
5)	N_5	x	14	=	0.05	x	B_5

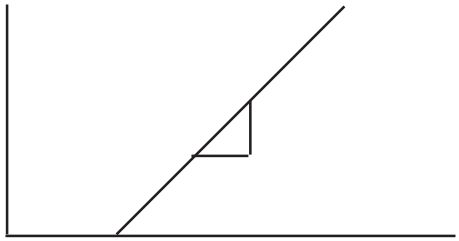
Normality of Oxalic acid (N) $= \frac{N_1 + N_2 + N_3 + N_4 + N_5}{5}$

Thus the exact normality of Oxalic acid can be found out. If we continue the titration to take 16 readings i.e. till 25 ml Oxalic acid is titrated, we can plot a graph of ml of NaOH added against ml of Oxalic acid taken. It will be a straight line.

$N\ V = N_2\ V_2$ (or) $V_2 / V = N / N_2$

Since v_2 / v is known by graph, N can be found out. The result obtained by graphical method is much more accurate than the result obtained by calculation

Slope $= V_2 / V$



ml. of Oxalic acid $\rightarrow$

Further, if we want to reduce the volume of solution used for the titration, we can use a microburette and take an interval of 0.5 ml or less instead of 1.0 ml for pilot reading. For the exact reading, we add the titrant solution drop by drop till we get the end point.

This method can be applied to all acid – base titrations with conventional indicators like phenolphthalein, methyl orange and bromothymol blue. The method can also be applied for redox titrations, iodometric titrations and other titrations where regeneration of indicator is

This method has the following advantages:

1. No solution is sucked by mouth so the method is safe.

2. Volume of solution required for the total titration is less.
3. Indicator is added only once.
4. Time required for the titration is less.
5. The results obtained by this method are more accurate than those obtained by the conventional method.

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