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Micro scale Experiments in Organic and Inorganic Chemistry

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ABSTRACT

Micro scale experiments in Organic and Inorganic Chemistry are of present importance. The methodology and analysis are given.

Semi micro 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 Fergusson 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.

Micro scale Preparations: To do preparations on a microscale, we need10ml/ 5ml R.B. flasks. B10 water condensers. The advantages of having the miniature apparatus are many. We can save on fuels as well as chemicals. When we use the B10 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 water 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.

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 semi micro 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 Pasture 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 immiscible 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 it 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

Test For Aromaticity: a. Substance burns with a smoky when introduced into the flame.
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.Nitration Test
b. Substance is added to a mixture of 3 drops of conc.sulphuric acid and 3 drops of con.nitric acid in a semi micro tube and warmed on a water bath for about 10 minutes. The solution is then poured into water.
Formation of an yellow precipitate or solution indicates the presence of aromatic compound.
Theory: The yellow colour is due to the formation of nitro compounds by the nitration of aromatic compounds.
Test for Unsaturation
a. To a little of the substance on a tile a drop of concentrated bromine water is added. Decolourisation shows the presence of unsaturation , decolourisation followed by turbidity formation shows the presence of aniline or phenol.
b. A pinch of the substance is taken on a tile. A drop of dil. potassium permanganate is added to it. decolouration indicates the presence of unsaturation or easily oxdisable compound formed
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: (Lassaigne's test)
Two small cut pieces of sodium are fused in a semi micro 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, 4drops of water are added. The first drop of water is allowed to react with excess of sodium. The second drop 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.

$NaCNS + 2Na \longrightarrow NaCN + Na_2 S$

Test for Nitrogen:
Test: 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 confirms the presence of Nitrogen.

THEORY: The extract on treating with ferrous sulphate solution forms sodium ferrocyanide.Upon treatment with conc.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:
Test: A drop of the extract is placed on tile. Add a drop of conc..nitric acid followed by a drop of silver nitrate solution . Curdy white precipitate indicates the presence of chlorine, pale yellow precipitate indicates the presence of bromine and Yellow precipitate indicates the presence of iodine

THEORY**:** .The extract is treated with conc. 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.
The halogens are precipitated as their silver halides.

$NaX + AgNO_3 \longrightarrow Ag\ X + NaNO_3$

Silver chloride forms an argentamine complex with ammonium hydroxide, which is soluble in excess of ammonium 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 of alcoholic silver nitrate on a water bath and acidified with a drop of conc.nitric acid. Immediate formation of a precipitate indicates the presence of halogen in the side chain. If no precipitate, then 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:

Test: A drop of the extract is mixed with a drop of sodium nitroprusside on a tile. Violet colouration indicates the presence of sulphur.

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

$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5 NOS]$
Sodium nitroprusside

A drop of the extract is tested with a drop of lead acetate solution on a tile. Black precipitate indicate the presence of sulphur

Theory: Sulphur gets precipitated as lead sulphide

$Na_2 S + Pb(OAC)_2 \longrightarrow PbS + 2\ NaOAC$

Solubility Tests:
Solubility of the substance in the following solvents are tested.

i. If **w**ater Soluble, then it shows the Presence of urea, carbohydrates etc.,
ii.If 5% Sodium bicarbonate soluble, then it shows the Presence of acids
iii. 5% Sodium hydroxide Soluble, then it shows the Presence of acids ,phenols
iv. 5% Hydrochloric acid Soluble, then it shows the Presence of amines

Action on Litmus:
When blue litmus paper is brought into contact with substance if it turns red, then it may be due to acids, phenols, etc.,
Red litmus turns blue may be due to amines.
Neutral may be due to Presence of carbohydrates, esters, carbonyls etc**.**

Action of Sulphuric Acid:

Test: About 5 mg of the substance is warmed with 3 drops of conc. sulphuric acid. If it chars with smell of burnt sugar, then it may be due to the presence of carbohydrates.
Theory: Carbohydrates are dehydrated completely by sulphuric acid leaving a charred carbon mass.
$\xrightarrow{Con.\ H_2SO_4} C_n(H_2O)_n \longrightarrow nC + nH_2O.$

Test for carboxylic acid:

Test: About 5 mg of the substance is treated with a drop of highly saturated sodium bicarbonate solution on a tile. Brisk effervescence shows the presence of carboxylic acid

Theory: Carboxylic acids react with bicarbonate to liberate carbon dioxide according to the equation.
$RCOOH + NaHCO_3 \rightarrow RCOONa + H_2O + CO_2\uparrow$

A drop of neutral ferric chloride solution is added to a little of the substance. Violet colour is due to presence of salicylic acid and Flesh colour is due to the presence of acids like phthalic.

Theory**:** As under phenols.

Test for ortho - dicarboxylic acid:
Test: About 5 mg of the substance is heated with an equal amount of resorcinol and 1 drop of conc. sulphuric acid in a semi micro tube. This mixture taken on the tip of a glass rod is immersed into about

20ml of dil. Sodium hydroxide in a beaker. Formation of green fluorescence is due to the 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. This is because the lactone ring is cleaved simultaneously to produce an anion comparable in structure to the anion produced from phenolphthalein.

Test for Phenol:

a.Neutral Ferric chloride Test

Test: A drop of the substance is mixed with a drop of neutral ferric chloride solution on a tile.
Violet colouration due to the presence of phenol chloride solution on a tile.

Theory: 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 conc. sulphuric acid in a semi micro 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 formation shows the presence of phenols.

Theory: Phenols react with phthalic anhydride to form phthaleins.. 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.

c. 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 indicates the 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.

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 is due to the 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. hydrochloric / 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 is formed due to the 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.

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 formation indicates the presence of 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 Beta-naphthol it gives the red azo dye.

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 semi micro 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 due to secondary amine.

Theory: The nitrous acid formed by the action of sulphuric acid on the nitrosamine 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.

Malachite green 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. Malachite Green dye is obtained due to the 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.

Test for nitro group:

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 semi micro tube, by heating for about 5 minutes with a drop of the supernatant liquid dye test is performed on a tile. Red azo dye Presence of. nitro compound (as under test for amines).
Theory:
The nitro compound is reduced to the primary amine by zinc dust and con.hydrochloric acid. With the primary amine dye test is performed.
Mulliken - Barker's test**:** About 3 drops of the substance and 3 drops of alcohol 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 due to the 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 soda lime. The resulting vapour is collected in another semi micro tube containing 5 drops of dil. hydrochloric acid. With a drop of the acid solution dye test is performed. Scarlet Red dye confirms the Presence of anilide

Theory: The anilides give out aniline vapours when heated with soda lime. 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 Presence of produced shows the presence of aliphatic 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.

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

Test for thiourea :

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 indicates the presence of thiourea
Theory: Thiourea may be decomposed by sodium hydroxide into hydrogen sulphide ,ammonia and carbamic acid. The hydrogen sulphide in solution may then react with lead acetate to form lead sulphide, which is obtained as a black precipitate.

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

Test**:** 5 mg 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 indicates the presence of thiourea.
Theory: On heating, thiourea forms a Biuret derivative. This forms an octahedral complex with iron as the central metal atom.

Test for Aromatic monoamide:

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. formed due to the 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 indicates the presence of sugars
Theory: as under α- naphthol

Test for aldehydes / ketones:

a. Borsche's reagent test: A drop of the substance or alcoholic solution of the ketone substance is placed on a tile. A drop of a concentrated solution of 2, 4 - DNP (Borsche's reagent) is added to it. Formation of red orange ppt, shows the presence of aldehyde or ketone.

Theory: The phenylhydrazine reacts with the carbonyl compounds to form their corresponding 2.4-dinitrophenylhydrazones.

b. 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 is due to the 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.

c. Fehling's Test**:** 2 drops or about 5mg of the substance is mixed with 2 drops of reducing Fehling A and 2 drops of Fehling B solutions in a Semi micro test tube. It is heated in a water bath for about 5 minutes. Red precipitate is due to the presence of aldehydes.

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 precipitated. This will be reduced to cuprous oxide by the aldehydes, there by getting themselves oxidised to carboxylic acids.

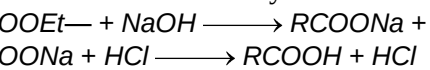
Test for ester:

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 and 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 confirms the presence of ester

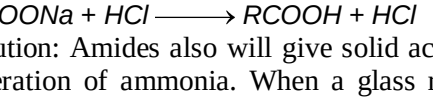
Theory: Ester reacts with hydroxylamine to give hydroxamic acid. This gives a deep violet colouration with aqueous Fe+3 ion, owing to the formation of a chelate complex.

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 confirms the 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 ⟶ RCOONa + EtOH



RCOONa + HCl ⟶ 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) 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 recrystallized from alcohol.

2) Phenyl Hydrazone: 1 g of phenylhydrazine hydrochloride and 1.5 g of and sodium acetate are dissolved in minimum amount of water. The solution is then added to 0.5 g 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
recrystallized 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 mixture is heated under reflux for about 15 minutes and then cooled in ice (If no precipitate separates on cooling, and then it may be diluted with 2-3 volumes of water)
4) Semicarbazone: 1 g of semicarbazide hydrochloride (H_2N-CO-$NHNH_2$.HCl) and 1.5 g of sodium acetate are dissolved in minimum amount of water. To this is added a solution of 0.5 g 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 recrystallized from alcohol.

For Amides:

(For ALIPHATIC diamides)
1) 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 recrystallized from dil. alcohol.

2) Oxalate Derivative: To a saturated solution of the substance, a saturated solution of oxalic acid is added slowly till a precipitate is formed. It is recrystallized from dil. alcohol.

(For AROMATIC Amides.)
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 recrystallized from hot water.

For Amines
1) 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 recrystallized from alcohol.

2) Bromo Derivative: 1 g 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 recrystallized from alcohol.

3) Acetyl Derivative: 0.5 g 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 20ml of water. The solution is boiled to decompose the excess acetic anhydride, cooled and filtered. It is recrystallized from alcohol.

$RNH_2 + AC_2O \longrightarrow RNHAC + HOAC$

For Secondary Amines:

Benzoyl and acetyl derivatives may be prepared using the same procedure as under primary amines.
Picrate derivative may be prepared using the same procedure as under hydrocarbons.

For Tertiary Amines:

Picrate derivative may be prepared using the same procedure as under hydrocarbons.

For Anilides :
1) Bromo Derivative may be prepared using the same procedure as under primary amines.

2) 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:

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 recrystallized from dil. alcohol.

For Carboxylic Acid:

1) 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 recrystallized from hot water.
2) 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 recrystallized from dil. alcohol acidified with dil. hydrochloric acid (This derivative is suitable for sulphonic acids also).

For Esters:
Acid Derivative**:** See test for esters.
For Hydrocarbons:
Picrate Derivative: Proceed as under test for hydrocarbons:
Nitro Derivative:
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 recrystallized from hot alcohol.

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 recrystallized from hot alcohol.

For Nitro Compounds: About 0.5 g 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:

1) 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.
2) Benzoyl Derivative: Proceed as under amines.

Inorganic Qualitative Analysis

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

Test for Halides: To about 3 - 5 mg of salt in a semi micro tube 3 drops of Con.H_2SO_4 with a glass rod dipped are added and heated. i. Colourless gas giving dense white fumes with a glass rod dipped in dil.NH_4OH. ii .reddish brown fumes presence of bromide. iii .violet vapours shows the presence of iodide. iv. Oily drops on the sides of the tube shows the presence of fluoride.

Test for Phosphate: 2-5mg 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 of Ammonium Molybdate taken in another test tube. Canary Yellow ppt. in the cold shows the Presence of Phosphate

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 shows the 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 shows the Presence of Borate.

For Basic Radical Analysis

Instead of doing elimination of interfering radicals, the residue obtained in sodium carbonate extract preparation 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 drop wise 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 drop wise 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. 0.05N) and NaOH (exact 0.05N).
Titre: Oxalic acid. Titrant: NaOH Indicator: Phenolphthalein. End Point: Colourless to pink.
Table: Titration of Oxaic acid Vs NaOH

Titre	Titrant
10 ml	B1
11 ml	B2
12 ml	B3
13 ml	B4
14 ml	B5

Calculation: N1V1

Oxalic acid NaOH

1) N1 x 10 = 0.05 x B1
2) N2 x 11 = 0.05 x B2
3) N3 x 12 = 0.05 x B3
4) N4 x 13 = 0.05 x B4
5) N5 x 14 = 0.05 x B5

Normality of Oxalic acid (N) = N1 + N2 + N3 + N4 + N5/5

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 = N2 V2 (or) V2 / V= N / N2

Since v2 / 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 = V2 / V ml. of Oxalic acid

Further, if we want to reduce the volume of solution used for the titration, we can use a micro burette 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 needed.

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.