



DAV College Jalandhar

B. Sc. Semester IV

Preliminary examination

Identification : molecular or ionic determining of organic chemical substance to distinguish from other compounds.

The identification of organic compounds by qualitative tests involves a study of chemical characteristics and the careful correlation of observed facts.

There are some methods use for identification the organic compounds.

- a- The systematic approach .
- b- Microscopic methods.
- c- Physical methods.

The first determined the Preliminary examination :

- Physical state

(solid , liquid)

- Color

- Colorless solids (Carbohydrates , Simple acid , Some phenols & Anilides)
- Colored solids (Nitro compounds , Amines , Phenols , Quinones)
- Colorless liquids (Alcohols , Aldehydes , Ketones , simple hydrocarbons , & simple acids)
- Colored liquids (Nitro compounds , Phenols , Amines)

- Odour

- Carbolic smell (Phenols)
- Smell of bitteralmonds (Benzaldehyde , Nitro benzene)
- Fruity pleasant smell (Esters)
- Spirtuons smell (Alcohols)
- Pungent smell (Formic acid & Formalin)
- Fishy pleasant (Amines)

Ignition test

Take a small portion of the given compound on a metallic spatula and ignite to over nonluminous flame and note the changes :

- a- Burns with a sooty flame (smoky flame) aromatic compounds .
- b- Yellow and non sooty flame (clear) aliphatic compounds containing alow percentage of carbon .
- c- Non inflammable compounds rich in halogen or containing a metal .
- d- Residual ash compounds containing a metal .
- e- Charring : Many organic compounds char , more particularly the following:
 - Carbohydrates (odour of burnt sugar) .
 - Tartaric acid and it's salts, Citric acid and it's salts.
 - Uric acid (odour some what resembling burnt sugar)
 - (salt of some acids char, although the free acids don't ,e.g. sodium succinate, lactate , and salicylate .)
- f- Charring with out melting (Boric acid , Starch , sulfonic acid)
- g- Violet vapours : contain iodine e.g. (Iodoform)
- h- Sublimation with a sugar smell (Oxamide)
- i- Evaporation of ammonia (nitrogenous compounds like Urea, Thiourea, Diamides) .

Division of compounds into Acids, Bases , Nutrals

To divide the compounds must be examine the solution of unknown by dissolve a small amount of solid substances in water or alcohol then put 1 drop of its solution on litmus paper and note change the colour of paper. Or adding 1 drop of phenolphthalen indicator to the solution unknown and note the change of this indicator. Through this examination divided the organic chemical to this list :-

Acidic	Basic	Nutral
*****	*****	*****
Carboxylic acids	Amines	Ethers
Phenols	Quinones	Aldehydes
Anhydrides	Hydrazines	Ketones
Cyano,Nitro acids	Imides	Esters
Amino acids	Quaternary ammonium salts	Carbohydrates
Acid halides	Urea	Hydrocarbons
Mercaptans	Pyridine	Amides
Thiophenol	Nitriles	
Sulfoxides		
Sulphonates		
Sulphates		
Sulphonic acids		
Alcohols		

Acids and Bases behavior

The inert organic compounds donot affected by use acids and bases e.g. Alkanes.

The organic compounds which have acidic groups dissolve in dil. NaOH solution.

The organic compounds which have basic groups dissove in dil. HCl solution like :

Dissolve in dli. NaOH

Dissolve in dil. HCl

Dissolve in conc. H₂SO₄

Sulphonic acid

Amines

Poly alkyl

(aromatic hydrocarbon)

Carboxylic acid

Pyridine

Must organic compounds

Contain oxygen atom

Phenols

Amides

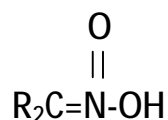
unsaturated hydrocarbons

Thiophenols

Anilines

Imides

Ar-SO₂-NH-R



R-CH=N-OH

R-C=C(COR)₂

|
OH

Oxidation reagent and bromine behavior

Most unsaturated organic compounds give positive test when treated with potassium permanganate solution. And the color disappeared.

1- Dissolve [0.1 gm or 0.1 ml] of organic compounds in water or acetone. Add [0.5 ml of dil. Sodium carbonate solution] , add (1-2) drops of KMnO_4 solution, note the change of permanganate color.

2- Bromine test :

Take [0.1 gm or 0.1 ml] of organic unknown and diluted by (1 ml) of water or CCl_4 . Add [2% bromine in CCl_4 solution (drop by drop)] and note the change of Bromine color.

- Fast disappeared in color without evolution of HBr. The unknown may be Unsaturated compounds .
- Disappeared in color with evolution of HBr gas, the unknown may be Aldehydes or ketones.
- White turbidity in solution with evolution of HBr gas, The unknown may be [phenols, Aromatic hydrocarbons, Enols].

Heating with soda-lime

Mix about (0.1 gm) of the unknown with about (1 gm) of powdered soda-lime, the odor of ammonia in the cold usually indicate an ammonium salt, that of chloroform indicates chloral hydrate. Place the mixture in a hard-glass test tube, close the tube by a cork and delivery tube, any liquid which subsequently condenses can not run back in to the hot part in the tube. Now heat the tube very gently at first and then more strongly. A non condensible product such as hydrogen or methane is the best detected by collecting the sample of the gas in a test tube condensible product. Such as benzene or phenol should be collecting by twisting the delivery-tube down wards and collecting the liquid in a few ml of water.

Substances	Class	Result
*****	*****	*****
Ammonium acetate (CH ₃ COONH ₄)	Ammonium salt	Ammonia evolved in the cold turn moist red litmus paper blue
Acetamide (CH ₃ CONH ₂)	Acid amide	Ammonia evolved
Urea (H ₂ N-CO-NH ₂)	===	=====
Glycine (H ₂ NCH ₂ COOH)	Amino carboxylic acid	Methyl amine evolved fish odour, alkaline reaction
Sodium acetate (CH ₃ COONa)	Carboxylic acid and salt	Methane evolved
Sodium succinate [CH ₂ (COONa) ₂]	Carboxylic acid and salt	Ethane evolved
Sodium benzoate (C ₆ H ₅ COONa)	Carboxylic acid	yield benzene (odour)
Sodium formate(HCOONa)	Carboxylic acid	Hydrogen evolved
Sbstances	Class	Result
*****	*****	*****

Sodium oxalate (COONa) ₂	Carboxylic acid	Hydrogen evolved
Sodium salicylate (HOC ₆ H ₄ COONa)	Carboxylic acid	yield phenol (odour) and also violet coloration when FeCl ₃ Added to aqueous solution odour of burnt sugar
Cane sugar (C ₁₂ H ₂₂ O ₁₁)	Carbohydrate	odour of burnt sugar
Tartaric acid [-CH(OH)COOH] ₂	some aliphatic hydroxy acid and	odour resembling burnt sugar
Citric acid [C ₃ H ₄ (OH)(COOH) ₂]	their salts	=== ===
Chloral hydrate [CCl ₃ CH(OH) ₂]		chloroform (characteristic odour, heavier than water)
Sulphanic acid [H ₂ NC ₆ H ₄ SO ₃ H]	Amino aromatic sulphonic acid	yield aniline (violet and then brown coloration with bleaching powder solution)
Anthranilic acid [H ₂ NC ₆ H ₄ COOH]	Amino aromatic carboxylic acid	yield aniline
Cinnamic acid [C ₆ H ₅ CH:CHCOOH]	unsaturated aromatic acid	some styrene colourless oily liquid, insoluble in water, pleasant odour
Uric acid [C ₅ H ₄ N ₄ O ₃]	purine	ammonia evolved

Summary of solubility behaviour

It is convenient to summarise the solubility characteristics of the commoner classes of organic compounds into seven groups as specified in the table bellow.

- 1- Compounds soluble in both water and ether. This includes the lower members of the various homologous series (4 - 5 atoms in a normal chain) that contain oxygen and / or nitrogen in their structures : they are soluble in water because of their low carbon content. If the compound is soluble in both water and in ether, it would also be soluble in other solvents so that further solubility tests are generally unnecessary. The aqueous solution should be tested with indicator paper. The test with sodium carbonate solution should also be performed.
- 2- Compounds soluble in water but insoluble in ether. These compounds with the exception of salts, are usually also soluble in dilute alkali and acid. The behaviour of salts to alkaline or acidic solvents may be informative. Thus, with a salt of a water-soluble base, the characteristic odour of an amine is usually apparent when it is treated with dilute alkali: like wise, the salt of a water-soluble, weak acid is decomposed by dilute hydrochloric acid or by concentrated sulphuric acid. The water soluble salt of a water- insoluble acid or base will give a precipitate of either the free acid or the base when treated with dilute acid or diluted alkali. The salts of sulphonic acids and of quaternary bases are unaffected by dilute sodium hydroxide of hydrochloric acid.
- 3- Compounds insoluble in water, but soluble in dilute sodium hydroxide. It should be recalled that some of the compounds belonging to this group are sufficiently strong acids to release carbon dioxide from sodium hydrogen carbonate (e.g. carboxylic acids, sulphonic and sulphuric acids, and certain substituted phenols)
- 4- Compounds insoluble in water, but soluble in dilute hydrochloric acid. It should be remembered that the hydrochlorides of some bases are sparingly soluble in cold water and one should therefore not be misled by an apparent insolubility of a compound (containing nitrogen) in dilute hydrochloric acid. The suspension in dilute hydrochloric acid should always be filtered and the filtrate made alkaline. A precipitate will indicate that the compound is indeed a base and should be included in this group.
- 5- Water-insoluble hydrocarbons and oxygen compounds that do not contain N or S and are soluble in cold

concentrated sulphuric acid. Any changes-colour, excessive charring, evolution of gases or heat, polymerisation and precipitation of an insoluble compound- attending the dissolution of the substance should be carefully noted. [alcohols; esters (but not ethyl benzoate; diethyl malonate or diethyl oxalate); aldehydes; methyl ketones; and cyclic ketones containing less than nine carbon atoms as well as ethers containing less than seven carbon atoms are also soluble in 85 per cent phosphoric acid].

6- Compounds, not containing N or S, insoluble in concentrated sulphuric acid. This test provides for a differentiation inter alia between alkanes and cycloalkanes and also simple aromatic hydrocarbons which are insoluble, and unsaturated hydrocarbons which are soluble in the reagent.

7- Compounds that contain N or S which are not in groups [1- 4] ; many of the compounds in this group are soluble in concentrated sulphuric acid. It will be observed that halogen compounds are not listed separately, but appear in each of the seven categories with their solubility behaviour.

Classification of organic compounds according to solubility behavior

1. soluble in both ether and water	2. soluble in water but in soluble in ether	3. soluble in 5% sodium hydroxide solution	4. soluble in 5% hydrochloric acid	5. Not containing N or S soluble only in concentrated sulphuric acid	6. Not containing N or S in soluble in concentrated sulphuric acid	7. Neutral compounds containing N or S
The lower members of the homologous series of alcoholic; Aldehydes; Ketones; Acids; Ethers; Phenols; Anhydrides; Amines; Nitriles; Poly hydroxy phenols.	Polybasic acids and hydroxy acids; Glycols; Polyhydric alcohols; Poly hydroxy aldehydes ;and ketones (sugars) ; some amides; amino acids; Di-and poly amino compounds; Amino alcohols; Sulphonic acids; Sulphinic acid salts.	Acids; Phenols; Imides; some primary and secondary nitro compounds ; Oximes; Thiols and thio phenols; Sulphonic acids; Sulphinic acids; Amino sulphonic acids; and sulphonamides; Some diketones and <i>B</i> - keto esters.	Primary amines; Secondary aliphatic and aryl –alkyl amines; Aliphatic and some aryl-alkyl tertiary amines; Hydrazines.	Unsaturated hydrocarbons; Some poly alkylated aromatic hydrocarbons; Alcohols; Aldehydes; ketones; Esters; Anhydrides; Ethers; and Acetals; Lactones ; Acyl halides.	Saturated aliphatic hydrocarbons; Cycloalkanes ; Aromatic hydrocarbons; Halogen derivatives of the above hydrocarbons; Diaryl ethers.	Nitro compounds (tertiary); Amides and derivatives of aldehydes and ketones; Nitriles; Negatively substituted amines; Nitroso, Azo, hydrazo, and other intermediate reduction products of nitro compounds; sulphones; sulphonamides of secondary amines; Sulphides; Sulphates; and other sulphur compounds.

Determination of melting point

The compound whose melting point is to be determined is powdered. A capillary tube approximately 2 inch length is sealed at one end by heating in a Bunsen flame. It is then filled up to about one cm (1cm) length with the powdered substance. The capillary is then attached to the lower end of the thermometer. The thermometer is now placed in a small beaker filled with paraffin oil or concentrated sulphuric acid such that the liquid covers at least the filled length of the capillary. The beaker is gently heated and rise in temperature is observed carefully. The temperature at which the solid has completely changed into liquid is also noted. This range of temperature is recorded as (m.p) range of substance.

Determination of boiling point

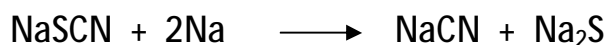
A few drops of the liquid whose boiling point is to be determined is taken in an ignition tube. A capillary tube sealed at the upper end is put inside the ignition tube and the latter is attached to the lower part of the thermometer with the help of a rubber thread. The thermometer along with the ignition tube is placed inside a Pyrex test tube in such a way that the test tube is covered by conc. H_2SO_4 . The temperature of the liquid in the test tube is carefully observed. The temperature at which a regular and speedy stream of bubbles begins to escape is taken to be the boiling point of the liquid this is recorded.

Detection of elements

In order to detect nitrogen, sulphur, and halogen in organic compounds. It is necessary to convert them into ionisable inorganic substance so that ionic tests of inorganic analysis may be applied. This may be accomplished by several methods, but the best procedure is to fuse the organic compound, with metallic sodium (Lassaigne's test). In this way sodium cyanide, sodium sulphide, and sodium halides, which are readily identified, if the above elements are present.



It is essential to use an excess of sodium, otherwise if sulphur and nitrogen are both present sodium thiocyanate NaSCN may be produced with excess of sodium the thiocyanate will be decomposed thus :



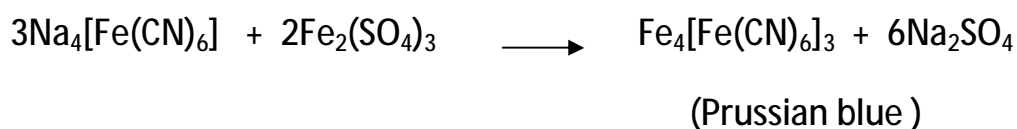
*Procedure for Lassaigne's test :

Place [4mm = 0.04gm] of freshly cut sodium in the dry tube have in readiness about (0.5gm) of the compound (if solid) or about (3 drops) of the compound (if a liquid). Heat the tube steadily until sodium vapor with is dark grey in color, for two minutes, and then allow it to coll.

Add about 0.5 ml of methanol to decompose any un reacted sodium and then add 5ml of distilled water. Boil gently for a few minutes to remove the methanol. Filter and use the clear, colorless filtrate for the various tests detailed below, if the filtrate is dark colored repeat the entire fusion procedure. Or by boil the dark filtrate with a little amount of charcoal and filter to produce the colorless filtrate.

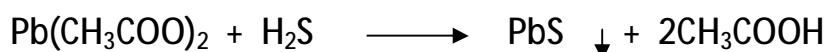
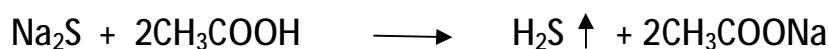
a- Detection of nitrogen :

Pour (2ml) of the filtered fusion solution in to a test tube containing (0.1- 0.2 gm) of powdered iron(II) sulphate to produce hexacyanoferrate (II). Heat the mixture gently with shaking until it boils to produce some iron(II) ions by the action of air. Then without cooling add just sufficient dilute sulphuric acid to acidify the solution and produce the iron(II) hexacyano ferrate (Prussian blue) .

b- Detection of sulphur :

This element may be tested for by either of the following two methods:

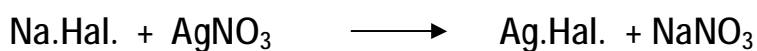
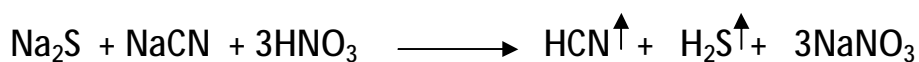
- 1- Acidify (1-2 ml) of the fusion solution with dilute acetic acid, add a few drops of lead acetate solution. A black precipitate of lead sulphide indicates the presence of sulphur .



- 2- To (1-2) ml of the fusion solution add (2-3) drops of a freshly prepared dilute solution (0.1%) of sodium nitroprusside $[\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}]$. Purple coloration indicates the present of sulphur.

c- Detection of halogens :

Acidify (2 ml) of the fusion solution with a drops of dilute nitric acid (boil the solution if the nitrogen and sulphur present) , add an excess of silver nitrate solution. Precipitate silver halides to indicates the present of halogen. If the precipitate is white , chlorine is present ; if it is pale yellow , bromine is present ; if it is yellow , iodine is present.



d- Detection of other elements present :

Less common elements are phosphorus, arsenic, antimony, mercury, or other metals which may be present as salts of organic acids. There is no direct method for the detection of oxygen. But by decomposition of these compounds to produce oxides or carbonates and then use an analytical methods to detect them.

Compounds contain [C , H , O]

1- Carboxylic acid [RCOOH]


Acetic acid (CH_3COOH) ; Benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$)

2- a/ Phenols ($\text{C}_6\text{H}_5\text{OH}$)

b/ Enols (Bromo acetone $\text{CH}_3\text{COCH}_2\text{Br}$)

3- a/ Aldehydes [RCHO] (Formaldehyde HCHO ; Benzaldehyde $\text{C}_6\text{H}_5\text{CHO}$)

b/ Ketones [RCOR] (Aceton CH_3COCH_3 ; Acetophenone $\text{C}_6\text{H}_5\text{COCH}_3$)

4- Quinones (p-benzoquinone) 

5- Alcohols [R-OH]

(Methanol $\text{CH}_3\text{-OH}$; Benzyl alcohol $\text{C}_6\text{H}_5\text{-CH}_2\text{OH}$)

6-Carbohydrates i.e (glucose ; fructose etc)

7-Esters [$\text{R-CO-OR}'$]

(Methyl acetate $\text{CH}_3\text{CO-OCH}_3$; Ethyl benzoate $\text{C}_6\text{H}_5\text{CO-OC}_2\text{H}_5$)

8-Ethers [$\text{R-O-R}'$]

(Dimethyl ether $\text{CH}_3\text{-O-CH}_3$; Methyl phenyl ether $\text{CH}_3\text{-O-C}_6\text{H}_5$)

9-Hydrocarbones [Alkanes ; Alkenes ; Alkynes & Arenes]

(Ethane $\text{CH}_3\text{-CH}_3$; Ethelene $\text{CH}_2\text{=CH}_2$; Ethyne $\text{CH}\equiv\text{CH}$;

Toluene $\text{C}_6\text{H}_5\text{-CH}_3$; Zylene $\text{CH}_3\text{-C}_6\text{H}_4\text{-CH}_3$)

Compounds contain [C , H , O , N]

1-Alkalies

a/ Amines [R-NH_2] (Ethyl amine $\text{CH}_3\text{CH}_2\text{-NH}_2$)

b-Hydrazines [R-NH-NH_2] (Methyl hydrazine $\text{CH}_3\text{-NH-NH}_2$)

2- Salts *[Ammonium salt] (Methyl ammonium chloride $\text{CH}_3\text{-NH}_3\text{Cl}$)

* [Ammonium salt of carboxylic acids] (Ammonium formate HCOONH_4)

3- *Nitriles [R-CN] * Amides [R-CO-NH_2] * Imides [$(\text{RCO})_2\text{NH}$]

4-Acyl bases [substituted amide on nitrogen atom]

5-Nitro compounds [R-NO_2] (Niro methane $\text{CH}_3\text{-NO}_2$; Nitrobenzene $\text{C}_6\text{H}_5\text{NO}_2$)

6-[Azo ; Azoxy ; Hydrazo ; Nitroso] Compounds (Hydroxyls of amine)

7-Derivatives of carbonyl groups :

- [Oxime] ($\overset{|}{\text{C}}=\text{NOH}$) * [Semicarbazons] ($\overset{|}{\text{C}}=\text{NHCONH}_2$)

8- Other compounds :

- *[Amino acids ; Amino phenols ; Amino alcohols ; Amino nitro compounds]
- *[Nitro acids ; Nitro esters ; Nitro aldehydes ; Nitro phenols]
- *[Cyano acids ; Cyano esters ; Cyano hydrines]
- *[Isonitriles ; Iso cyanates ; Nitrates ; nitrites]

Compounds contain [C , H , O , Halogens]

1- Simple alkyl & aryl halides

(Chloro benzene $\text{C}_6\text{H}_5\text{Cl}$; Ethyl chloride $\text{CH}_3\text{CH}_2\text{Cl}$)

2- Substituted halides [Halogenated acids ; Halogenated Phenols]

3- Acid halides (Acetyl chloride CH_3COCl ; Benzoyl chloride $\text{C}_6\text{H}_5\text{COCl}$)

Compounds contain [C , H , O , S]

1- Mercaptanes & Thiophenols [R-SH ; Ar-SH]

2- Thioethers [R-S-R] ; Disulphides [R-S-S-R]

3- Sulfoxides [R-SO-R]

4- Sulfones [R-SO₂-R]

5- Sulfates [R-OSO₂-OR] & Alkyl hydrogen sulfates [R-OSO₂-OH]

6- Sulfites [R-OSO-OR]

7- Sulfonates esters [R-SO₂-OR]

8- Sulfonic acids [R-SO₂-OH]

Functional group identification

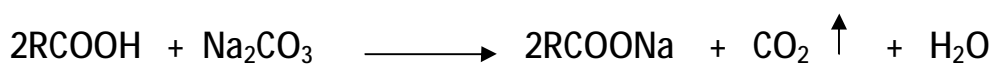
The solubility behavior of unknown, elemental analysis, spectroscopic methods are used to identify the functional groups of compounds. Any group has some tests to identify it.

Compounds contain [C , H , O] only :-

1-Carboxylic groups [-COOH]

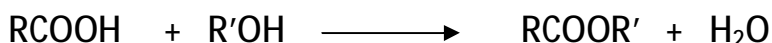
a-Soluble in Na_2CO_3 solution with the evolution of CO_2 gas .

Sodium carbonate or sodium bicarbonate solution prepared by dissolving (5% aqueous alcohol + 5% sodium bicarbonate). Add a few drops of reagent To (0.05 gm of sample) , note the evolution of bubble of gas.



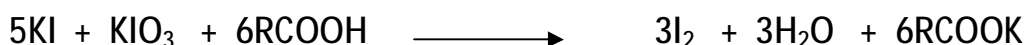
b- Ester formation :

Heat gently (0.5 ml) of ethanol or methanol with 0.25 gm of the acid and a few drops of conc. H_2SO_4 for about 1 minute. Cool and pour into a few ml of water in a test tube and note the odor. The esters formation have a special best odor.



c-Ioden test :

(4-5) drops of an aqueous or an alcoholic solution of the acids in to the test tube. Add {0.5 ml of 2% KI solution} + {0.5 ml of 4% KIO_3 solution}. Heat the mixture in a boiling water bath for (2 minutes). Cool the content and add (2-3) drops of an aqueous starch. Blue or purple is appeared.



a- Place about (0.25 gm) of the acid in a boiling test tube and add a slight excess of ammonia solution until just alkaline to litmus paper. Boil until odor of ammonia is completely removed. To the cold neutral solution add a few drops

of neutral FeCl_3 solution. A raddish – brown precipitate of ferric hydroxide is appeared.



2- Phenolic groups [Ar- OH]

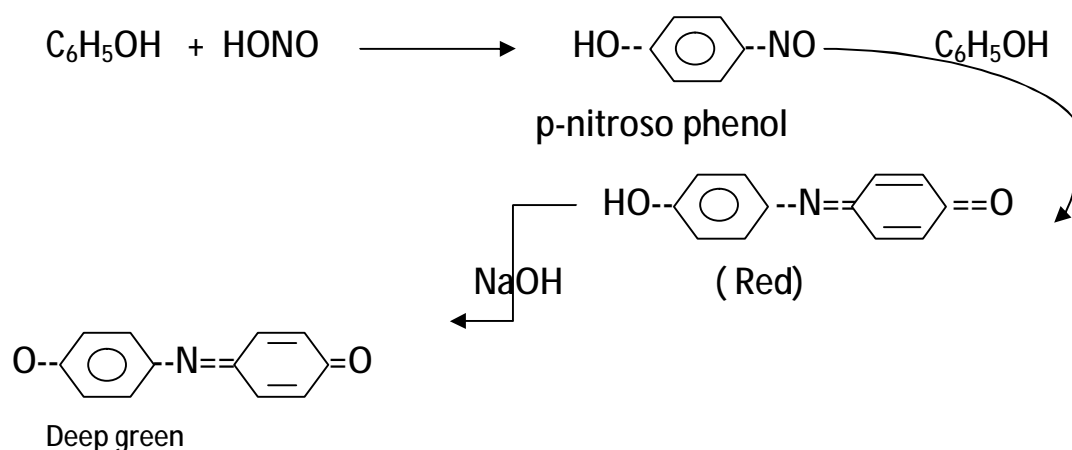
a- Ferric chloride reaction :

Dissolve a few crystal of unknown in water and add a few drops of ferric chloride solution. A violet coloration is produced.

b- Dissolve a few crystal of unknown in methanol and add some drops of methanolic ferric chloride (5gm of ferric chloride in 100 ml of methanol) A violet of blue or green coloration is produced. This result prove that the unknown is one of the undissolve phenols in water.

c-Liebermann test :

To (1 minute crystal of sodium nitrite) in a clean dry test tube add(0.25 gm) of phenol and heat very gently for about (20 second); allow to cool and add twice volume of conc. H_2SO_4 on rotating the tube slowly in order to mix the content a deep green or adeep blue coloration develops after (1-2) minutes.dilute cautiously with water ; the solution turns red. Now add an excess of NaOH solution, the green or blue coloration.



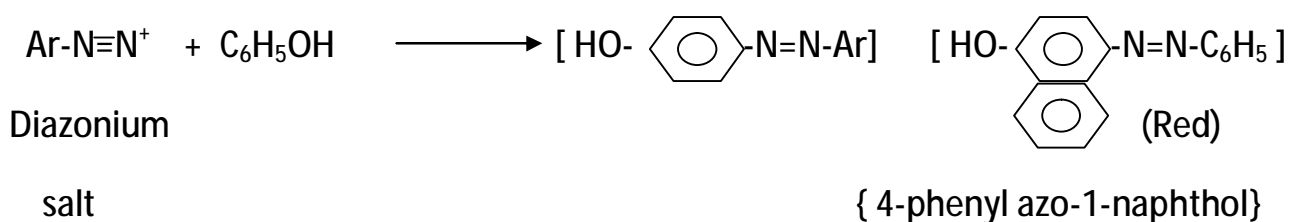
d- Azo dyes formation :

Dissolve (2-3) drops of aniline in (1 ml of conc. HCl)(and add 3 ml of water. Shake

to dissolve any hydrochloride which may have separated and cool in ice. Add a few drops of (20% sodium nitrite solution). Add this cold diazonium solution to a cold solution of the phenol in an excess of aqueous NaOH solution. Solutions or precipitates of azo- dye ranging in colour from orange through scarlet to dark red according to the phenol used are obtained.

Note : in particular that 1- Naphthol gives a brown – red ; 2- Naphthol a scarlet

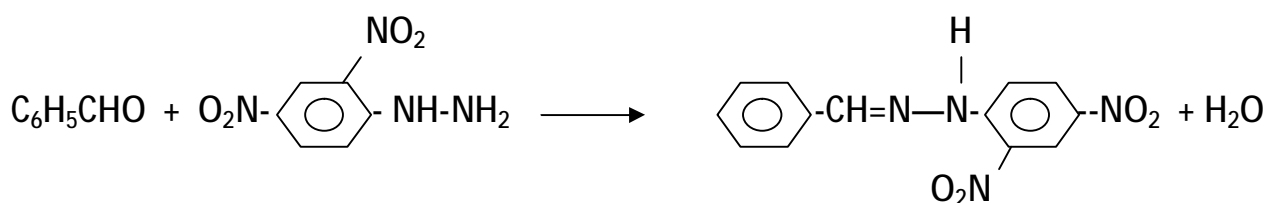
Precipitate ; Catechol decomposes.



3-Identification of aldehydes & ketones

a-Brady's reagent

To a few drops liquid unknown or conc. solution of solid unknown in methanol ,add A few drops of 2,4-dinitro phenyl hydrazine reagent (dissolve 2,4 -dinitro phenyl hydrazine in 5M of HCl). A yellow or orange precipitate is produced in the cold form (2,4- dinitro phenyl hydrazone) this result is indication about presence of carbonyl group in aliphatic aldehydes or ketones and red or dark yellow precipitate is produced when the carbonyl group in aromatic aldehydes or ketones.

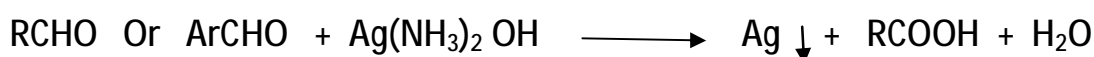


Chemical differentiation between aldehyde & ketones by :-

b- Tollen's test :

Aldehydes alone reduce Tollen's reagent and produce a silver mirror on the inside of the test tube [add 2-3 drops (0.05gm) of the compound to (1-2ml) of Tollen's reagent contained in a clean test tube] if no reaction appears to take place in the cold, warm in a beaker of hot water.

Note : Tollen's reagent is prepared as follows : dissolve [1 gm of silver nitrate in 10 ml of water] (solution A) and [1 gm of NaOH in 10 ml of water] (solution B) when the reagent is required mix equal volumes 1 ml from A & B in a clean test tube and add dilute ammonia solution drop by drop until the silver oxide is just dissolved.



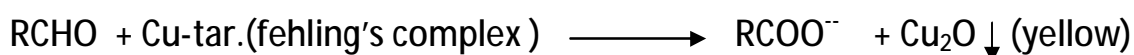
c-Fehling's reagent :

Aldehydes alone reduce Fehling's solution to yellow or red copper (I) oxide. Use 2 drops or (0.05 gm) of compound and (1-2 ml) of Fehling's solution. Heat on boiling water bath for (2-4 min.). This test is positive for aliphatic aldehydes, but is often indecisive for aromatic aldehydes.

Note : preparation of Fehling's solution :

Solution (A): dissolve (3.46 gm) of copper (II) sulphate crystals in water containing a few drops of dilute sulphuric acid, and dilute the solution to (50 ml).

Solution (B) : dissolve (6 gm) of pure sodium hydroxide and (17.3 gm) of pure Rochelle salt [sodium potassium tartarate] in water and dilute the solution to (50ml). keep the two solutions separately in tight stoppered bottles and mix exactly equal volumes immediately before use.



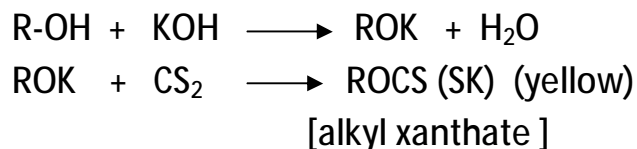
d- Sodium nitroprusside solution :

Aliphatic ketones containing the [CH_3CO-] groups give a red coloration with alkaline sodium nitroprusside.

4- Identification of alcohols [R-OH]

a- Xanthate test :

Add a small piece of (KOH) to (0.25 ml) of unknown in test tube. Heat the mixture until (KOH) is dissolved cool the test tube and add (1ml) of ether then drops of carbon disulphide (CS₂). Pale yellow precipitate will appear.



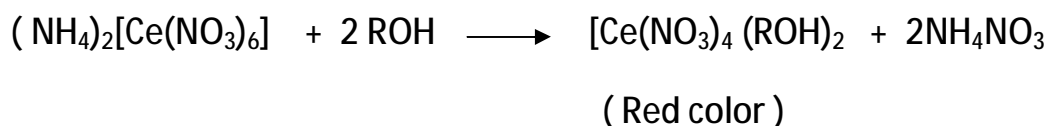
b-Chromic acid :

Add (1 drop) of sol. (CrO₃ ; or K₂CrO₇ dissolve in con. H₂SO₄) to the (0.05ml) Of unknown , heat the mixture , converted the orange color to blue-green Color . this test consider the indication about a presence of primary or secondary alcohols.

c-Ceric ammonium nitrate solution :

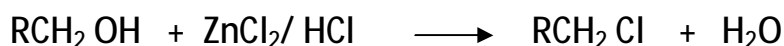
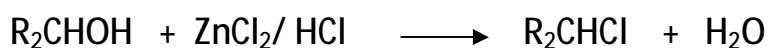
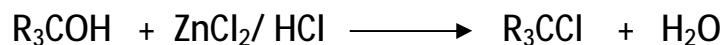
Dissolve (0.1 gm) of unknown in water or dioxan. Add a few drops of ceric ammonium nitrate solution [prepared from dissolve 1 gm of ceric ammonium nitrate in 25 ml of 5 M HNO₃]. A red color is obtained for the simple alcohol, where as poly alcohol i.e glycerol a faint red color obtained.

Note : the mono or disaccharide obtain a red color and disappeared after short time.



d-Lucas's test :

Add (0.25 ml) of alcohol in the test tube , add (2-5 ml) of lucas reagent [dissolve of $ZnCl_2$ in conc. HCl] closed the test tube with stopper and shake gently for (1 min.) then leave the solution , if oily layer is appear, this unknown is tertiary alcohol when the oily layer is appear after (5-10 min.) this unknown is secondary alcohol, where as after (10-15 min.) this unknown is primary alcohol.



5-Identification of carbohydrates :

a- Molish's test :

Dissolve about (0.1gm) of the carbohydrate in (2ml) of water, add (2-3 drops) of 1% ethanolic -1-naphthol , add then carefully pour (2ml) of conc. H_2SO_4 down the side of test tube so that it form a heavy layer at the bottom . a deep violet coloration is produced where the liquids meet.

b- Sulphuric acid test :

Warm about (0.1 gm) of the carbohydrate with (.05 ml) of conc. H_2SO_4 , observe the immediate blackening. As the temperature is raised , CO_2 ; CO ; SO_2 are evolved.

c- Fehling's test :

Use (0.05 gm) of the compound and (1-2 ml) of fehling's solution. Heat on boiling water bath for (5 min.) , a red copper (I) oxide will appeared .

This test use to identify reduced mono ; disaccharide i.e. (maltose ;lactose)

d- Barfoed test :

Dissolve the carbohydrate in water , add a few drops of [6 % cupric acetate dissolve in 1 % acetic acid] boil gently for (2min.) a red precipitate of copper (I) oxide will appear , this test identify the mono saccharide and if mixture needs more than (5 min.) the unknown is disaccharide.

e- Osozone test :

Dissolve (0.5 gm) of carbohydrate in (2.5 ml) of water. Add the prepared solution [2ml of phenyl hydrazine dissolved in about 3 ml of glacial acetic acid] shake the mixture well and heat it in a water bath for about (30 min.) cool the reaction mixture where osazone gradually begins to precipitate out. Filter and allow it to dry on a porous plate. Compare about the crystal of the saccharide by the microscope.

f- Tauber's test :

This test is used to compare about penta & hexasaccharide. Add some drops of (4% benzidine in glacial acetic acid) to (0.1 gm) of carbohydrate. Boil for (1 min.) yellow to brown coloration for hexasaccharide and a red coloration for pentasaccharide is appeared.

g- Pinoff's test :

This test is used to identify ketonic hexasaccharide i.e. [fructose]. To about (1 ml) of (1% fructose) solution in boiling tube. Add an equal volume of a freshly prepared (4% aqueous solution of ammonium molybdate) and then (1 drop) of glacial acetic acid. Heat the boiling tube in a boiling water bath A greenish blue colour with (3- 4 min.) is obtained.

h- Identification of starch :

To (1 ml) solution of the compound in water , add a few drops of iodine solution. A deep blue colour is obtained which disappears on boiling but reappears on cooling.

Note : A red to brown colour is obtained in the presence of dextrine.

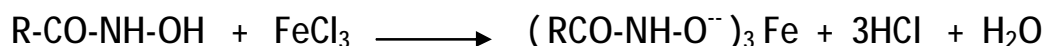
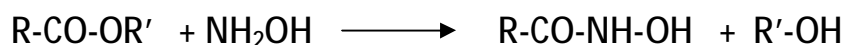
i- Identification of cellulose :

This compound dissolved in cuprammonium hydroxide solution and precipitate when acidify.

6-Identification of esters and anhydrides :

a- Hydroxamic acid formation :

To a few drops of an ester add (0.2 gm) of hydroxyl amine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) and about (5 ml) of [10% NaOH] solution and gently boil the mixture for (1-2 min.) . cool and acidify with dil. HCl and then add a few drops of ferric chloride solution. A violet or deep red-brown colour develops immediately. Similar coloration is given by anhydrides.



- Identification of acid anhydrides only :

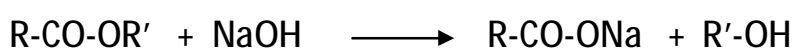
Dissolve (0.05 gm) of the organic unknown in chloroform add a few drops of aniline. Boil the mixture gently for (1-2 min.) , precipitation is happened.

- Identification of esters only :

By hydrolysis test :

Dissolve (0.25 gm) of ester in (0.5 ml) of alcohol ,add (2-3) drops of dil. NaOH solution and (1-2) drops of phenolphthalein. A pink color is obtained now put the test tube in boiling water bath for aboute (5 min.) the pink color disappears .

Phenolphthalein is pink colored so long as the medium is alkaline when the alkali is consumed dueto hydrolysis of ester the pink color dissappears.



7-Identification of quinones :

- All quinones yellow or orange yellow color identify by visual examination.
- Dissolve a few crystals of quinones in (10% aqueous NaOH) solution and shake gently. The solution turns rapidly brown and then almost black owing to atmospheric oxidation .
- By acidified potassium iodide. To an aqueous KI solution containing a few drops of dil. H_2SO_4 . add (1ml) of aqueous benzoquinone solution , iodine is liberated by brown in color. (Especially the low oxidation number of poly cyclo or alkylic quinones).

8-Identification of ethers :

a- Iodine solution :

Dissolve 1 crystal of iodine in ether and note the brown color is obtained.

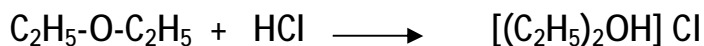
Note: Aromatic hydrocarbon e.g. (benzene) give purple solutions .

b- Ester formation :

Heat under very efficient reflux (0.5 ml) of ether ,(2 ml) of glacial acetic acid and (1 ml) of conc. H₂SO₄ for (10 min.) distil (1ml) of liquid. Smell the ester odor. Use a few drops of this liquid for the hydroxamic acid test for esters.

c- Oxonium salt formation :

Shake up (0.5ml) of ether with (1ml) of conc. HCl or conc. H₂SO₄ , and note that a clear solution is obtained owing to the formation of water – soluble oxonium salt .



Note : Aromatic and aliphatic hydrocarbons do not behave in this way.

9-Identification of alkenes & alkynes :

a- Potassium permanganate :

Place (2 drops) of organic unknown in a test tube , add some drops of (1% Potassium permanganate solution) , shake it gently , note the color of permanganate disappeared, this unknown may be one of alkenes or alkynes.

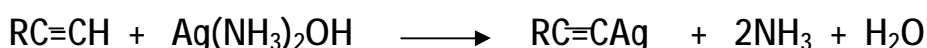
b- Bromine solution :

Dissolve the unknown in CCl₄ , add (2-3 drops) of (5% bromine in CCl₄) , note the brown red color of bromine disappeared with out evolution of HBr gas.

c- Tollen's test :

Shake some drops of unknown with tollen's reagent , a white precipitate on in side of test tube is happened , this test is identification about alkynes mono substituted [RC≡CH] . this salt decomposed with (10% HNO₃) .

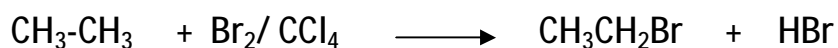
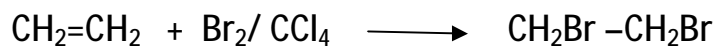
Note: Don't heat this salt because explosive is happens.



Identification of organic compounds with Bromine or permanganate

No.	structures	Perman ganate	Br ₂ Addition	Br ₂ substitution
1	Alkene & alkynes	P	P	N
2	ArC≡CAr & Ar ₂ C=CAr ₂	p	N	N
3	Phenols, aromatic amines	P	N	P
4	ketones	P	N	P
5	Some of aldehydes	P	N	P
6	Pri. & sec. alcohols	P	N	N
7	Mercaptanes & Disulphides	P	N	N
8	Thiophenols	P	N	P

Note : The substitution reaction with Br₂ evolution HBr gas.



Compounds contain [C , H , O , N]

When nitrogen is present :

1- Amides : [--CO—NH₂]

a- Sodium hydroxide solution:

To (0.2 gm) or (0.5 ml) of unknown, add (1 ml) of aqueous NaOH, Ammonia is evolved, this can be detected by its smell and by its action on moist. Red litmus paper.

Note : this test used to identify amines, amides and imides.

2- Amines:

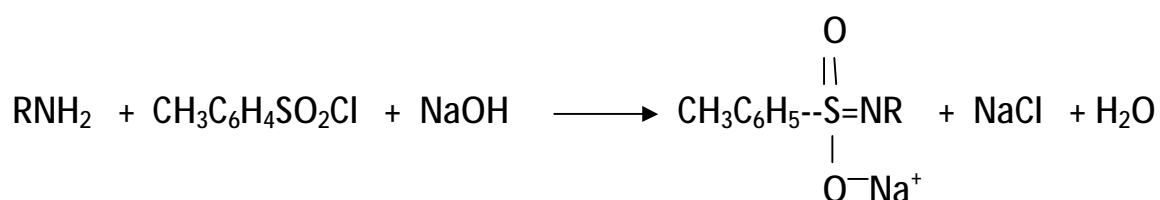
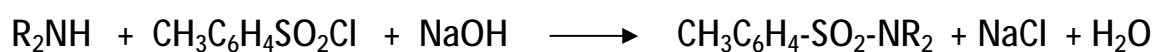
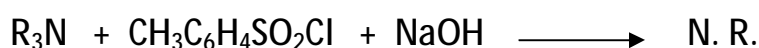
a- Rimini's test for aliphatic amines :

*Dissolve (2 drops) of amine in (1 ml) of acetone, add (3 ml) of water and then (2 drops)of (1% sodium nitroprusside solution), a violet color is appeared through (2 min.) if the primary aliphatic amine is present.

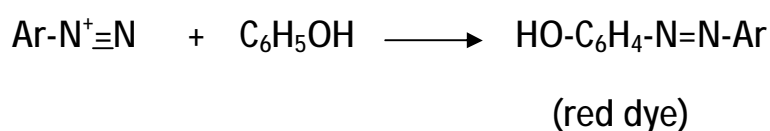
*Dissolve (2 drops) of amine and (2 drops) of acetaldehyde in (3 ml) of Water, then add (2 drops) of (1% sodium nitroprusside solution). A blue Color is appear through (2 min.), in the present of secondary aliphatic amines.

b- Hinsberg's test :

For distinction between [pri. , sec. , and ter.] amines , to a few drops of amine . add few drops of (p-toluene sulphonyl chloride) , add few drops of dil. HCl then add few drops of dil. NaOH solution in order to the medium become alkaline, then distill by steam to separate the tertiary amine. Cool the mixture and filtrate the derivative of secondary amine, or by extracted with ether then acidify the filtrate with dil. HCl to get the derivative of primary amine, filtration it.



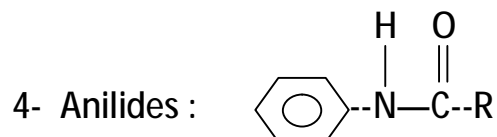
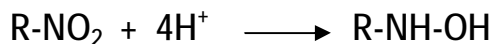
c- Distinction between aliphatic and aromatic primary amines. By formation diazonium salt when react the aromatic amine with nitrous acid , which be detected by formation of red dye with alkaline phenol solution .



3- Nitro compounds :

*Mulliken barker test :

In a test tube , take about (0.1 gm)of compound , (2ml)of alcohol. (0.5 ml NH_4Cl solution), add a pinch of zinc dust, boil , cool and filter, add to filtrate (1 ml of tollen's reagent) , a grey or black of silver mirror is produced. The reduction of nitro group is happen .



* Tafel's test :

Take (0.1 gm)of unknown , add (2 ml of conc. H_2SO_4) and shake , add (0.1 gm) of powdered potassium dichromate. A red or violet color which changes to green on standing. Shown the presence of an anilide

Compounds contain [C , H , O , N , S]

1- Thioureas :

a- Sodium hydroxide :

Simple thiourea upon boiling with NaOH solution , gives of ammonia.

b- Lead acetate :

Boil a little amount of the substance with dil. NaOH solution. Cool and add lead acetate solution. A brown color or black of precipitate indicates the compound to be a thioureas.

2- Amino sulphonic acid : [Contain -NH_2 ; -SO_2 groups]

Diazonium formation :

Dissolve a little of the unknown in dil. HCl. Cool and add NaNO_2 solution so as to complete the diazotization. Now add alkaline solution of B-naphthol. A red or orange dye is formed .

Compounds contain [C , H , O , Halogen]

These compounds divided in to :

1- Simple alkyl or aryl halides:

All heavier than , and insoluble in water, all liquids, except iodoform . which is a yellow crystalline solid. The remained are colorless liquids when pure.

- A fire retardants when the compound contain higher quantity of halogen.

a- Silver nitrate solution :

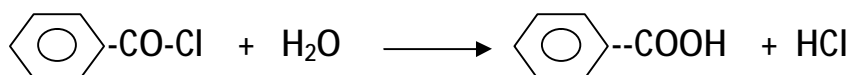
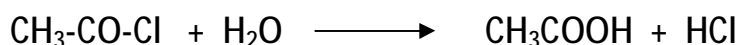
Boil (0.1 ml) of the unknown with (1 ml of alcoholic NaOH solution) for about (10 min.). Cool , dilute the solution with water , add excess of dil. HNO_3 , and then AgNO_3 solution. A precipitate of silver halide is obtained.

Note: the aromatic halogen compounds depends on the type of additional functional group present.

2- Substituted halide e.g. [esters ; alphahydrogen ketones ; benzyl halides]

3- Acid halides :

Have a fuming volatile , toxic, corrosive and hydrolysis with water to carboxylic acid and hydrogen halides.



Compounds contain [C , H , O , S]

*Almost mercaptans ; thioethers ; disulphides ; esters of sulphuric acid are liquids and reminds are solids .

*Mercaptans and thiophenols have corrosive fuming , but thioethers ; disulphides have mild odor or unpleasant odor .

*Sulphonic acid ; alkyl hydrogen sulphate dissolve in water to get acidic solution. But some of natural sulphur compound undissolve in water and dissolve in ether.

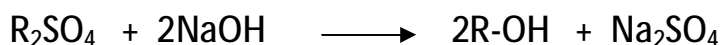
*Sulphonic acid ; alkyl hydrogen sulphate dissolve in sodium bicarbonate solution to evolved CO_2 gas.



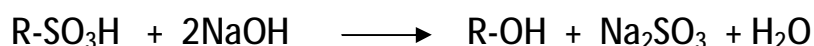
*Mercaptans ; thiophenols ; thioethers ; disulphides ; sulphoxides remove the color of permanganate when they react with potassium permanganate .

*Dissolve in alkaloids :

- Mercaptans and thiophenols react with alkali solution to get mercaptide which hydrolysis by aqueous to give mercaptan by dilution, Alkyl sulfate hydrolysis by (10% NaOH solution to sodium sulphate and alcohol :



-sulphonic acid esters also hydrolysis by NaOH solution to sodium sulphonate and alcohol :



*Nitroprusside test :

Use to identification of mercaptans and thiophenols.

Dissolve a small amount of unknown in dil. Ammonia solution , add a few drops of (5% sodium nitroprusside) ared – purple colour is appears immediately when the unknown is mercaptan.