Qualitative Analysis of Organic Compounds

The analysis and identification of unknown organic compounds constitutes a very important aspect of experimental organic chemistry.

Qualitative organic analysis is an experimental science that provides methods of identifying an organic substance.

Methods for identification;
- Systematic approach
- Microscobic methods
- Physical methods
- Chromatographic methods
- Spectroscopic methods

In general, the analysis of an organic substance is carried out in the following order;

*Determined physical characteristics - solid, liquid, colour and odour.
* Perform an ignition test
* Analysis for elements present
* Perform solubility tests and find out in which solubility class
* Determine the boiling point or melting point.
* The functional groups of the substance are identified and, if necessary, their derivatives are prepared and their melting points are determined.
* Special reactions of the suspected substance are applied by using the substance monographs
* The Rf value is calculated (Chromatography).
* UV, IR, NMR, Mass spectra are examined.

This analysis process is discussed in more detail below in order. Rf analysis, elemental analysis and spectroscopic methods with searching procedures are not mentioned here because it is described in other sections.

PHYSICAL PROPERTIES OF SUBSTANCES

The substance to be analyzed may be solid, liquid or gaseous. Since gaseous substances exhibit some difficulties in working and these are very few of the organic compounds, they will not be emphasized here.

The following properties are required for liquid and solid substances:
* Taste
* Odor
* Color
* Solubility

<u>Taste:</u> Organic substances have their own unique taste. The toxicity of many substances indicates that this feature is not required. However, the determination of taste with a small amount of substance in the experiment may not cause toxicity. Sometimes it is possible to take a toxic dose without realizing it.

Bitter taste: Alkaloids (quinine, morphine, strychnine), quinoline derivatives, glycosides, polyethylene glycol derivatives, barbital, ureites.

Sweet taste: Carbohydrates, chloroform, glycol, resorcin, sucrose, sodium salicylate, phenol, *etc.*

Salty taste: Formic acid and acetic acid salts, urea, urethane etc.

Burning taste: Chloralhydrate, certain acids, benzoic acid, salicylic acid, resorcin, phenols.

Sour taste: Organic and inorganic acids (vitamin C).

The substance which make numbness in the tongue: Local anesthetic compounds (cocaine, benzocaine, novocaine, pentocaine, lidocaine, etc.).

Odor: Many organic substances have a characteristic odor. The smell of the substance may indicate which class is a compound. In order to determine this, it should be tried beforehand which odor of the compounds of various classes. The odors of alkalines, esters, phenols, amines, aldehydes and ketones are different. When the substance is more volatile, its smell is more noticeable.

For example; coumarin, eugenol, vanillin, ethyl acetate, methyl salicylate, phenols, thymol, menthol, ethanol, acetone, ether, chloroform, amyl alcohol and pyridine have unique odors. Sulfur compounds have a rotten egg smell. For example, mercaptans and isonitrile have very unpleasant odors. Benzaldehyde, nitrobenzene and the like smell like bitter almonds.

If a substance has a very noticeable and penetrating odor, it can be considered to be a volatile, small molecule.

Color: An examination of color can sometimes give important information about the structure of matter. A variety of functional groups may be suspected if the substances are colored. Carbon, hydrogen, oxygen and sulfur-containing substances are colorless. However, quinones, unsaturated side-chain ketones, and very few saturated diketones are colorful among these. If the substances are colored, there is the presence of nitrogen. Nitrogen-bearing colored compounds include the following: Substituted anilines, toluidines, polycyclic amines, hydrazines, nitro or nitroso or aminophenols, polynitro or polyamino hydrocarbons, nitro or aminokinones, azo and diazo compounds, picrates, ozazones, hydrazones, etc. In all these compounds the color changes from yellow to red.

The number of double bonds in the molecule and the groups such as =C=O, =C=S, O=N=O, -N=N-, -N=O also have an effect on color. The substances with the *o*- or *p*-quinonoid structure, or in other words, the substances only with chromophore groups, are generally yellow colored. If the substance contains a chromophore group as well as an oxochrome groups such as NH_2, -NHR, -OH or ,SH, the color becomes darker.

Homogeneity: If the substance is solid, a certain degree of homogeneity control is done by examining the amount of a few mg of matter under a magnifying glass or microscope. It is seen that a substance that appears homogeneously with the naked eye might be a mixture of colored and colorless components under the microscope. Likewise, when the substance that appears to be the only type with the naked eye is enlarged, it can occur that there is a mixture of amorphous and crystal components or other kinds of crystals.

Determination of pH of the substance: The pH of the substance can also give some ideas about that substance. Because some of the functional groups it contains can give acidic or basic properties. The substance must be soluble in distilled water for the determination of pH. If it does not dissolve, the mixture is heated and sufficiently solubilized for pH even if it is not dissolved in the heat. Then red or blue litmus paper determine the acid, base or neutral character.

Solubility: It is based on molecules or inter-ionic forces applied by both solvent and solute. In order to dissolve a substance in a solvent, it is necessary to loosen some bonds in both the solute and the solvent and to form new bonds between the dissolved ions or molecules and the molecules of the solvent. If a substance is dissolved in 1 ml of solvent at room temperature up to 30 mg, this substance is dissolved in that solvent.

The following table 1.1 shows the resolution state with the amount of solvent that one part of the substance can be dissolved:

The amount of solvent in which one part of solute is dissolved	Resolution status
Less than 1 part	very soluble
1-10 parts	easy soluble
10-30 parts	soluble
30-100 parts	slightly soluble
100-1000 parts	sparingly soluble
1000-10000 parts	very hard soluble
More than 10000 parts	practical insoluble

Solubility experiments should be carried out at normal room temperature. Although many substances are not dissolved in normal temperature, they can be soluble with heat. The same is also true for liquids. In this case, it is necessary to mix the liquid with the solvent and not to form two phases. By looking at the solubility of an unknown substance in the solvents given below, an idea about the unknown substance can be obtained in three aspects (water, ether, 5% hydrochloric acid, 5% sodium hydroxide, 5% sodium bicarbonate, sulfuric acid, phosphoric acid).

-The solubility indicates the presence of the functional group. For example, if hydrocarbons are partially soluble in water we can understand that they might have a functional group in their structure because they are not soluble at all.

- The solubility in certain solvents gives more important, specific information about the functional group. For example, benzoic acid is dissolved in 5% sodium hydroxide, although it is insoluble in water. Thus, the dissolution of a water-insoluble substance in sodium hydroxide solution indicates a strong acidic group in its structure.

-Referring to the solubility of an organic substance, we can also obtain an idea of the molecular weight of the substance. For example, in the homologous series with monofunctional groups, compounds with 5 carbon atoms or less are dissolved in water and compounds with a high number of carbon atoms are insoluble in water.

Solvents can be grouped into two classes;

*Nonpolar solvents

*Polar solvents

Acidic substances are dissolved in weak basic medium, basic substances are dissolved in weak acidic medium.

There is a principle ”Similar solves similar”. Nonpolar substances are soluble in nonpolar solvents, polar substances are soluble in polar solvents. If it is a low-chain substance then its nonpolarity decreases.

As the hydrocarbon portion of a molecule grows, the properties of the substance will be similar to the properties of hydrocarbons, the solubility in water will decrease, whereas the solubility in ether will increase. this also applies to aromatic hydrocarbons.

In the case of a phenyl ring is present in any part of an aliphatic acid, alcohol or an aldehyde molecule, the effect of this ring on solubility is equivalent to the action of an aliphatic radical carrying 4 carbon atoms.

In polymorphous substances, the low melting point polymorph has greater solubility in water.

The solubility of small molecular weight substances in water is greater than that of large molecules. However, there are some cases that do not comply with this rule; For example, amides of the type $R-CO-NH_2$ are less soluble than the $R-CO-N(R1)_2$ derivatives.

Since the growth of molecular weight or the formation of the polymer of organic substances will increase the intermolecular force, the solubility in water and ether will decrease.

Halogen entry into a structure is also one of the factors reducing water solubility. If the halogen enters the organic structure in salt form, the solubility in water increases.

A branched carbon chain-bearing substance is better soluble in water than its straight-chain isomers of the same molecular weight.

The place of the functional group in the carbon chain also affects the solubility; the closer the homogeneous group is to the middle of the molecule, the higher the solubility in water.

The solids must be finely powdered to increase the dissolution rate. The solubility of the substances given as samples in laboratories shall be made according to the solubility table given below. Thus, the solubility group of the substance will be determined. Determining the solubility group of the substance as previously described above will give us an idea of the structure and functional groups of that substance.

Solubility Group Determination:

GROUP 1: Generally, compounds with monofunctional groups of 5 or less carbons.

Only if C, H and O are present: Carboxylic acids, alcohols, aldehydes, ketones, anhydrides, esters, ethers.

-If nitrogen is present: Amides, amines, nitriles, oximes.

-If halogen is present: halogen substituted compounds of compounds given in (a).

-If sulfur is present: heterocyclic hydroxy sulfur compounds, mercaptoacids, thioacids.

-If nitrogen and halogen are present: halogenated amines, amides and nitriles.

-If nitrogen and sülfür are present: sulfurated heterocyclic amino compounds.

GROUP 2: Only if C, H and O are present: Dibasic and polybazic acids, hydroxy acids, polyhydroxy alcohols.

- If nitrogen is present: Aminoalcohols, amino acids, amines, urea.

- If halogen is present: Haloacids, haloalcohols, aldehydes.

- If sulfur is present: Sulfonic acids.

- If both nitrogen and halogen are present: amine salts of halogenated acids.

- If both nitrogen and sulfur are present: amino, nitro, cyano sulfonic acids.

GROUP 3: Amines, amino acids, aryl-substituted hydrazines, N,N-dialkylamides.

GROUP 4: Generally 10 or less carbon compounds:

- Only if C, H and O are present: Acids and anhydrides.

- If nitrogen is present: Amino acids, heterocyclics, carboxylic acids.

- If halogen is present: Haloacids, acid halides.

- If sulfur is present: Sulfonic acids, Mercaptans.

- If both nitrogen and sulfur are present: Sulfonamides, aminosulfinic acids.

- If both sulfur and halogen are present: Sulfonhalides.

GROUP 5:

- If there is only C, H and O are present: phenols, enols, some high-molecular weight acids.

- If nitrogen is present: Aminophenols, nitrophenols, cyanophenols, oximes.

- if sulfur present: Thiols, thiophenols. halofenols.

- If nitrogen and halogen are present: Polynitro halogenated aromatic hydrocarbons, substituted phenols.

- If nitrogen and sulfur are present: Sulfonamides, aminothiophenols.

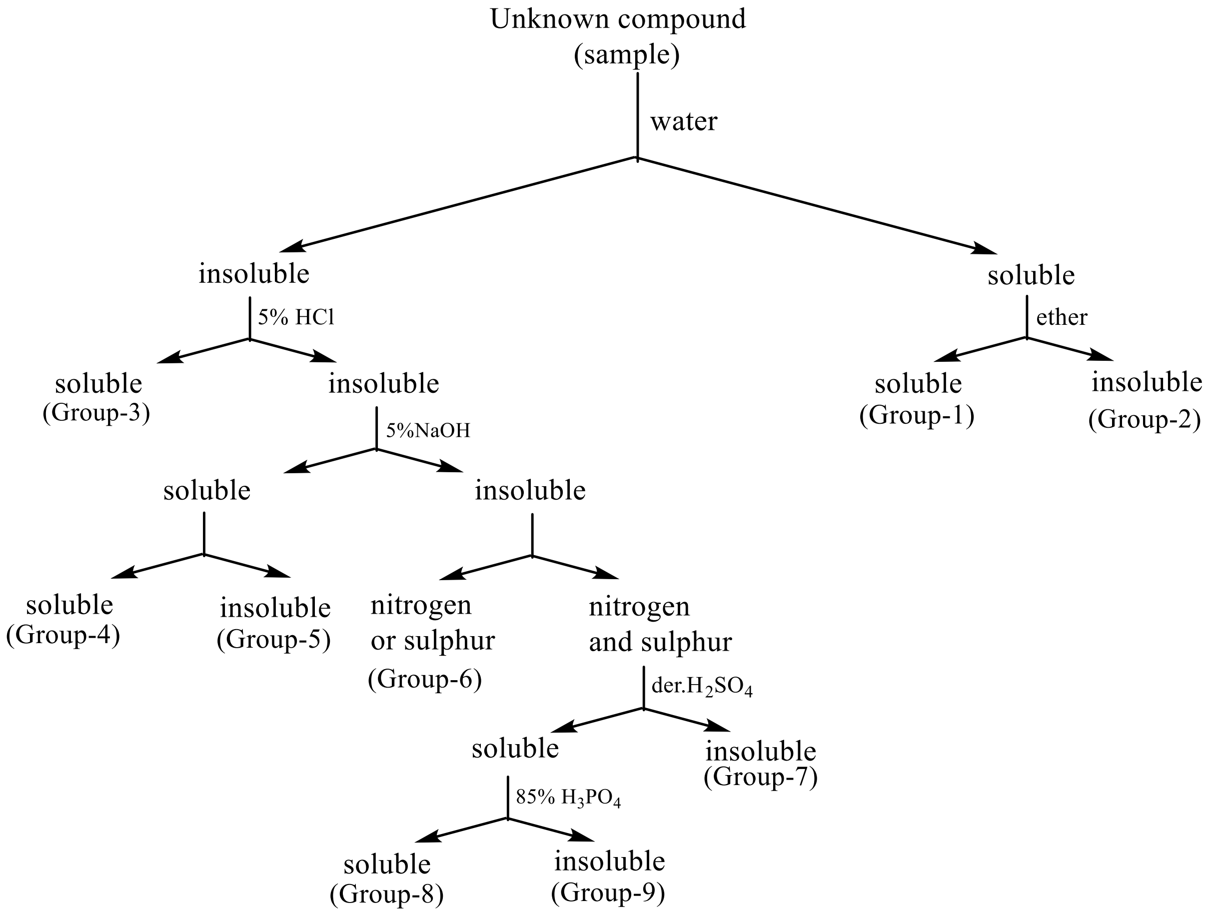
GROUP 6:

- If nitrogen is present: Amides, diarylamines, nitriles, triarylamines.
- If Sulfur is present : Sulfides, sulfones, thioesters.
- If nitrogen and sulfur are present: thiourea derivatives, sulfonamides, thiocyanates.
- If nitrogen and halogen are present: halogenated amide, amine and nitriles.

GROUP 7: Halogenated derivatives of hydrocarbons and hydrocarbons.

GROUP 8-9: Neutral compounds not containing nitrogen and sulfur.

Procedure to determine the solubility groups of substances is given in below table 1.2



IGNITION TEST

0.1g of the substance is heated in a porcelain crucible with a light flame. The substance is checked for flames, whether the substance is flammable, then the flame is gradually increased and burned strongly. The changes in the item now will be evaluated as follows.

*Ammonia smell:*Ammonium salts, urea and urea derivatives, hexamethylenetetramine.

No burning residue and caramel smell during combustion: Tartaric acid, citric acid, dextrin, starch and so on.

Mercaptan smell: Sulfonal, trional, thiourea derivatives *etc.*

Phenol odor: Phenol, phenolic compounds.

Brown vapors: Bromine, nitrogen dioxide.

Purple vapors: Iodine.

Acid reaction: Volatile acids.

Alkaline reaction: Volatile alkalis.

Burning with clear, almost blue flame: substances carrying oxygen.

Burning with bright flame: Olefins, cycloparaffins.

Burning with yellow, dull, very few flames: Aliphatic hydrocarbons.

Yellow and sooty flame combustion, the residue consisted of coal initially: aromatic hydrocarbons are relatively more than the number of carbons.

White colored burning residue: metal salts of organic acids.

ELEMENT ANALYSIS

All organic substances have C and H. Since the determination of C and H requires special experiments, these elements will not be searched. However, the search for nitrogen, sulfur and halogen in organic substance must be done. These 3 elements will be searched in laboratory studies.

Carbon Search (Carbon Test)

Copper Oxide (CuO) test: A small amount of substance is mixed well in a small test tube with a few solids of CuO. (CuO should be rescued from organic residues by heating dry to dry method in a tube). In the mouth of the tube, a glass pipe that is curled twice in the right angle with the help of a cork stopper is passed; the free end of the tube is immersed in a tube with barite water (barium hydroxide). Now the tube containing the mixture of substances and CuO is heated strongly, exhaled gases (CO2) cloud the barite water (BaCO3), which indicates the presence of carbon.

Hydrogen Search (Hydrogen Test)

In the above copper oxide reaction, in the cold parts of the tube collected water droplets indicate the presence of hydrogen.

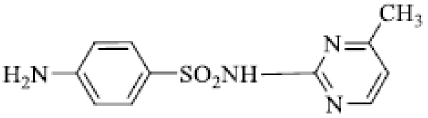
0.1 g of the analysis sample is mixed with some Na_2SO_3 or $Na_2S_2O_3$ and heated strongly; if hydrogen is present, H_2S occurs (H_2S can be recognized by its smell and blackening of lead acetate paper).

Nitrogen Search (Nitrogen Test)

The one part of (1K) sample is mixed with six part of (6 K) of soda lime. It is heated in a crucible from the bottom with asbestos fire on the asbestos wire. The nitrogen in the organic substance becomes inorganic and leaves in the form of ammonia vapors. If the wetted red litmus paper turns blue, the presence of nitrogen is understood.

$$\text{Org N} \longrightarrow \text{Inorg N} \longrightarrow NH_3 \xrightarrow{\text{water}} NH_4OH^+$$

Example:



The important point to be considered in this experiment is the soda lime is also a very strong basic compound. Splashes during heating may turn the litmus paper to blue. But in this case, the change in the colour of litmus paper occurs in the form of dots. However, in the presence of nitrogen, the paper is wetted and the whole of the portion extended to the crucible becomes blue. For this reason, during the experiment, the inclusion of the litmus paper should be kept in the mouth of the crucible.

Soda Lime Preparation: One part (1K) calcium oxide is mixed with one part (1K) sodium hydroxide. Leave two days to become watery. It is heated in the open flame, until it becomes powder or granules.

Halogen and Sulfur Search (Halogen and Sulfur Test)

These elements must also be made inorganic before the search for halogen and sulfur. Therefore, before the search the organic structure is hydrolyzed with heat, potassium nitrate and sodium carbonate. 1 K potassium nitrate is put into a crucible for the experiment and the crucible is heated from the bottom. After potassium nitrate is completely melted, 2K potassium nitrate, 2K sodium carbonate and 1 K sample are added again. The mixture is melted by heating with air gas from the bottom. Thus, the sulfur sulphate anion and halides are converted into halide anion. After that the mixture is cooled. Add some distilled water and transfer to two separate tubes with stirring. Sulfur in one of these tubes, the other in the halogen are searched.

Determination of Sulfate Anion

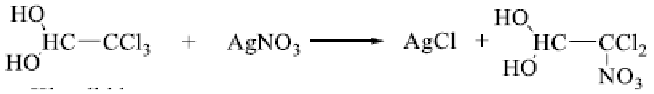
The solution in the tube is acidified with 10% hydrochloric acid solution and 10% barium chloride is added to the tube. A white precipitate is indicate the presence of sulfur anion and by this sulphur as well. In the meantime, the ions like carbonate, which may be present in the environment, can be precipitated as well so some more hydrochloric acid solution is added. Because the precipitates to be formed from other anions are dissolved in hydrochloric acid.

$$SO_4^{-} + BaCl_2 \longrightarrow BaSO_4 + 2Cl^{-}$$

precipitate

Determination of Halide Anion

10% nitric acid solution and 10% silver nitrate are added to the melting solution in the tube. The formation of precipitates indicates the presence of halides and hence halogen. Nitric acid should be added in large amounts for the reasons described in the search for sulfur.



$$(HO)_2HC-CCl_3 + AgNO_3 \longrightarrow AgCl + (HO)_2HC-CCl_2(NO_3)$$

Chloral hydrate

Since most of the organic substances contain halides as salts, the test given above must be repeated directly to the sample. Because the halides are in the form of salt and they are not organic, they give the reaction without melting. For this, the sample is dissolved in some amount of water and tested.

DETERMINATION OF FUNCTIONAL GROUPS

After physical determinations and elemental analysis, functional groups are analyzed and the following characteristics are considered. Analysis is not for an ion but a part of the molecule. These groups may not be obtained by the action of the entire desired molecule. Now let us examine the functional groups that will be determined in the laboratory.

Tests for Unsaturation

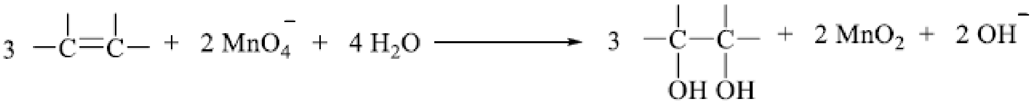
Two common types of unsaturated compounds are alkenes and alkynes characterised by the carbon-carbon double and triple bond, respectively, as the functional group. Bonds must necessarily be between carbon atoms.

The two common qualitative tests for unsaturation are the reactions of the compounds with (a) potassium permanganate, and (b) bromine in carbon tetrachloride.

Ethylenic hydrocarbons (-C=C- reactions):

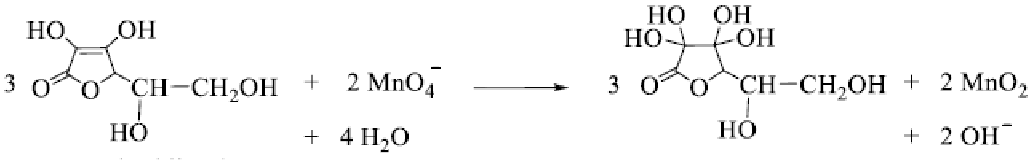
Bayer Test: Permanganate solution shows the oxidizing effect on double bonds. It converts them into glycol derivative first and then by the complete cleavage of the bond to ketone or aldehyde. In alkaline hydroxide or alkali carbonate solutions, potassium permanganate oxidizes the double bond and it is reduced to manganese dioxide. If the compound containing unsaturation is insoluble in water, its solubility in alkali is examined, and if the compound is an unsaturated acid, it will dissolve in an alkaline acid. Among the organic solvents, the most suitable ones for this reaction are pyridine, acetone and benzene. Although this detection reaction with permanganate generally yields good results, it is important to note that some reducing groups which do not contain unsaturation but which remove the color of the permanganate should not be forgotten. Some compounds of basic character may neutralize neutral or alkaline permanganate solutions even if they do not carry double bonds, however, they are resistant to acidic solutions.

Experiment: In neutral solutions, an amount of the compound is taken to control the unsaturation of the compound and dissolved in an appropriate selected solvent, potassium permanganate is added dropwise and shaken after each addition, if there is an unsaturation, the purple color disappears. A brown precipitate consisting of manganese dioxide may be formed, and a purity test may be required because the impure saturated organic solvents spend some permanganate also.



$$3\ -\overset{|}{C}=\overset{|}{C}-\ +\ 2\,MnO_4^-\ +\ 4\,H_2O \longrightarrow 3\ -\underset{OH}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-\ +\ 2\,MnO_2\ +\ 2\,OH^-$$

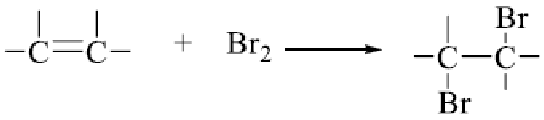
Example:



Ascorbic acid

Bromine Test: The reaction between the unsaturated compounds and the bromine takes place in the form of an addition reaction to the double bonds. While making this reaction, the substance to be searched for its double bonded and the bromine should preferably be dissolved in the same solvent. The most suitable solvent is glacial acetic acid. If the substance does not dissolve in acetic acid, it is dissolved in carbon tetrachloride, chloroform, carbon sulfide, ether or nitrobenzene.

Experiment: The compound is dissolved in a suitable solvent. 2% bromine solution is added. After shaking well, loss of yellow color of bromine is a sign of unsaturation. If the bromine consumption exceeds 10 drops, the compound is phenol, amine, enol, aldehyde or ketone.



Antimony trichloride Test: Unsaturated substances produce colors ranging from yellow to red or brown with a 30% solution of $SbCl_3$ in chloroform.

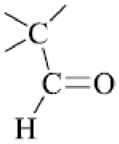
Concentrated Sulfuric Acid Test: Most of the ethylenic and aromatic hydrocarbons can be identified by concentrated sulfuric acid. Concentrated sulfuric acid is added to the solution of the substance in alcohol or acetic acid anhydride. If there is an unsaturated group, a red, blue or purple color will occur. Ketones or aromatic hydrocarbons carrying the methoxy group also color with concentrated sulfuric acid.

Acetylenic hydrocarbons (-C≡C- Reactions):

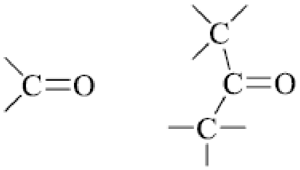
Acetylenic bonds are very similar to olefinic bonds in terms of chemical reactions. The unsaturation character of them can also be determined by addition reactions in olefins. A condition that is characteristic for acetylenic bonds is the water addition. This addition proceeds against mercury-II-sulphate and sulfuric acid and -C≡C- turn into -CO-CH2-. Identification can be made by this aldehyde or ketone.

CARBONYL GROUP

The carbonyl group is a functional group formed by oxygen bound to carbon atom.



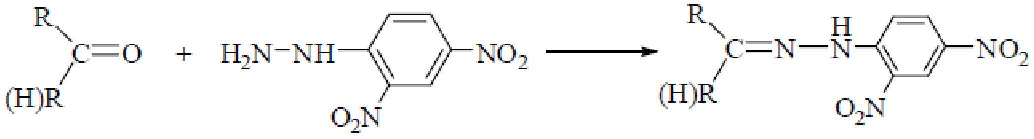
Aldehyde



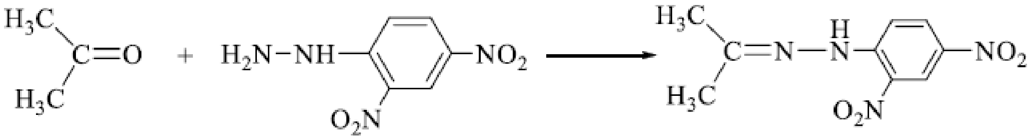
Ketone

2,4-Dinitrophenylhydrazine Test:

Aldehyde and ketone group gives both this reaction. A quantity of sample is dissolved in 1 ml of methanol and a saturated solution of 2,4-dinitrophenylhydrazine prepared in 5 ml of 2N hydrochloric acid solution is added. Shaken vigorously. If the precipitate does not form, the mixture is boiled. Again shaken. The yellow or orange precipitate indicates the presence of the carbonyl group.



Example:



Acetone

<u>Color Reaction:</u> Prepare the following mixture on a watch glass:

-1 drops of unknown substance

-1 drops of pyridine

-1 drops of 5% sodium nitroprussiyat (% 1)

-1 drops 2 N NaOH

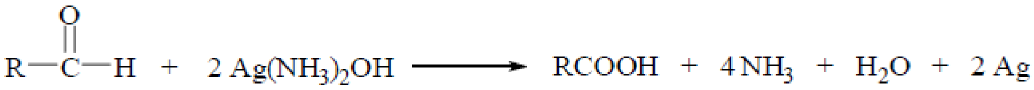
The formation of yellow-red color indicates the presence of the carbonyl group.

<u>Reduction Reaction:</u> A small amount of unknown substance is treated with a few drops of 1% alcohol methylorange solution. The formation of yellowish-red color shows the presence of carbonyl group.

<u>Separation of Aldehyde and Ketone Groups:</u> Sugars, aldehydes, polyhydroxyphenols, hydroxycarboxylic acids, diketones, primary ketals, sulfinic acids, aminophenols, alkyl and aryl hydroxylamines, certain aromatic amines, hydrazo compounds and hydrazines, reduce "ammonia silver nitrate solution" to elemental silver.

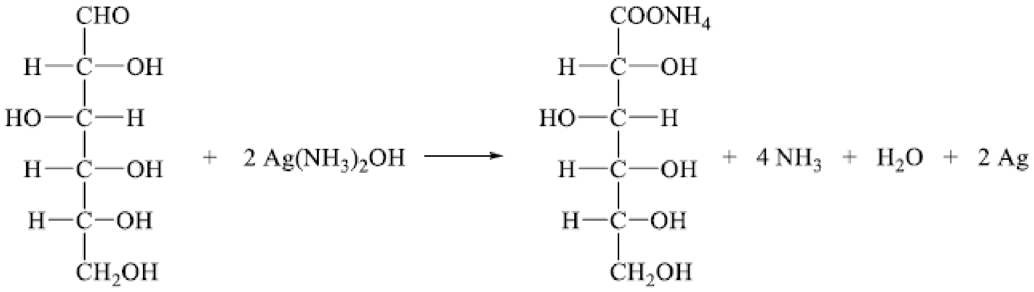
<u>Tollen Test:</u> Aldehydes reduce the Tollen reagent (Ammonia $AgNO_3$ solution) to form a silver mirror on the inside of the test tube. Ketones are ineffective.

Experiment: A quantity of the substance is treated with Tollen reagent, held in a 70-80 ° C in water bath. If there is aldehyde in the structure, silver is separated.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + 2\,Ag(NH_3)_2OH \longrightarrow RCOOH + 4NH_3 + H_2O + 2\,Ag$$

Example:



Glucose

Preparation of Tollen's Reagent:

3g Silver nitrate dissolve in 30 ml water (Tollen A)

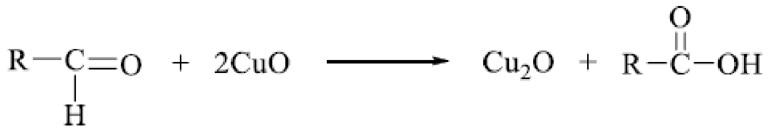
3g Sodium hydroxide dissolve in 30 ml of water (Tollen B)

The two solutions are mixed in equal amounts and a dilute ammonia solution is added dropwise until the formed silver oxide is dissolved.

Fehling Test: Aldehydes, reduce Fehling solution to red copper-I-oxidized reductase. Ketones are ineffective.

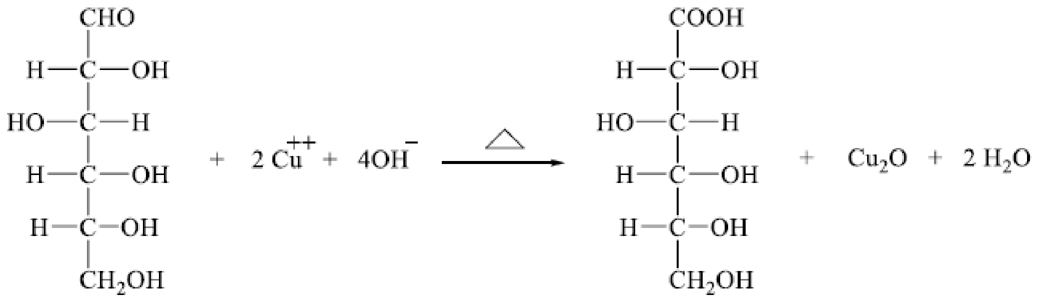
Experiment: A sample is dissolved in 0.5 ml of water and 1 ml of Fehling solution is added.

The mixture is heated to boiling. If there is aldehyde, red copper-I-oxide precipitates.



$$R-\underset{\displaystyle H}{\underset{|}{C}}=O + 2CuO \longrightarrow Cu_2O + R-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

Example:



Glucose

Preparation of the Fehling solution: Fehling solution is obtained by mixing equal amounts of Fehling A (cuprous sulfate, sulfuric acid and water) and Fehling B (sodium-potassium tartrate, NaOH and water) solutions.

As it needs to be prepared fresh, Fehling A and B solutions will be given as ready and mixed in equal amounts during the experiment.

ESTER AND ANHYDRİDE GROUPS

The ester and carboxylic acid anhydrides form hydroxamic acid with hydroxylamine. All hydroxamic acid solutions form red-violet colored complex salts with iron-3-chloride solution.

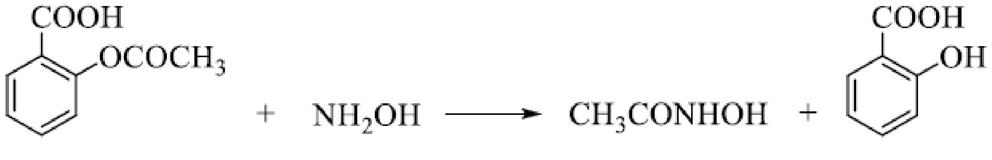
Ferri hydroxamate Test: Mix the same amount of saturated methanolic potassium hydroxide solution with 0.5 N hydroxylamine hydrochloride solution prepared in 95% ethanol. Sample is added to the mixture and boiled in water bath. Chilled and acidified with N HCl (checked with litmus paper). To the mixture an iron-3-chloride solution is added dropwise. Red-violet color indicates the presence of ester or anhydride group.

$$\underset{\text{ester}}{RCOOR'} + NH_2OH \longrightarrow RCONHOH + R'OH$$

$$\underset{\text{anhidrit}}{RCOOCOR'} + NH_2OH \longrightarrow RCONHOH + R'COOH$$

$$3\ RCONHOH + FeCl_3 \longrightarrow \underset{\text{Colored compound}}{(RCONHO)_3Fe} + 3\ HCl$$

Example:



Aspirin

$$3\ CH_3CONHOH + FeCl_3 \longrightarrow (CH_3CONHO)_3Fe + 3\ HCl$$

ALCOHOL GROUP

The alcohol group is a hydroxyl group attached to a carbon atom. It is generally shown as ROH. The alcohol group can be primary, secondary or tertiary.

Xanthate Test: Primary and secondary alcohols give alkyl xanthates with alkaline hydroxides and carbon sulfide at room temperature. The xanthates of the tertiary alcohols are easily hydrolyzed. In addition, the test tube must be completely dry, since the alkyl xanthates are very easily dissolved in the water.

Xanthogenate Formation: 1 drop of unknown substance, 10 drops of ether, 2 drops of CS_2, thoroughly crushed pellet NaOH or KOH is shaken vigorously and allowed to stand for 5 minutes.

Then add 1-2 drops of 1% aqueous ammonium molybdate solution and shake until all NaOH is dissolved.

It is then acidified with 2N H_2SO_4. Blue-violet color or precipitate formation indicates the presence of primary or secondary alcohol.

$$R{-}OH + CS_2 + KOH \longrightarrow R{-}O{-}C({=}S){-}S^-,\ K^+$$

Chromic Acid Test: 1K compound is dissolved in acetone or acetic acid. 5% CrO_3 solution prepared in 3N H_2SO_4 is added and heated slightly. Green color indicates the presence of alcohol.

In aliphatic hydrocarbon molecules, those having small molecular weights of alcohols which are formed by the introduction of hydroxyl groups in place of one or more hydrogens, are similar to water in terms of physical properties, *ie* polar compounds such as water. In terms of structure, alcohols are primary, secondary and tertiary.

Bordwell-Wellman Test: 1K compound is dissolved in acetone. One drop Bordwell-Wellman reagent is added and stirred. After a while the blue-green color occurs. Aldehydes, phenols, enols such as compounds that are easily oxidizable, disrupt this reaction. If there is an impurity in the tertiary alcohols, a small amount of precipitate may form. But the orange color of the indicator remains unchanged. In primary and secondary alcohols, this orange color changes completely.

$$R{-}CH_2OH + CrO_3 \xrightarrow{H_2SO_4} R{-}CHO + Cr_2(SO_4)_3$$

Example:

$$CH_3CH_2OH + CrO_3 \xrightarrow{H_2SO_4} CH_3CHO + Cr_2(SO_4)_3$$

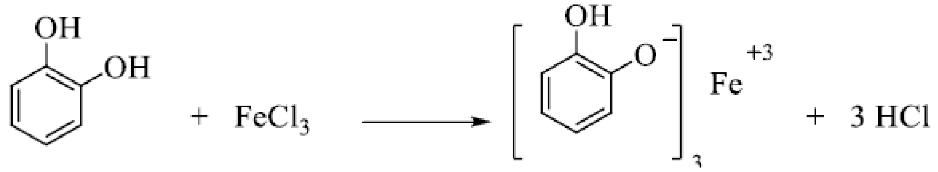
Preparation of Bordwell-Wellman Reagent: 1 g of CrO_3 is dissolved in 1 ml of concentrated H_2SO_4 and the mixture is made up to 3 ml with water.

PHENOL GROUP

The phenol group is a hydroxyl group attached to one of the carbon atoms in the aromatic ring. Phenols give blue, green, blue and black color with iron-3-chloride solution. Some substances, although they do not contain phenol group, may also give a red color with iron-3-chloride solution.

Experiment: Some substance is dissolved in water in the test tube. 5% iron-3-chloride solution is added dropwise. The colors above indicate that the experiment is positive. The mechanism of the reaction in the experiment has not yet been described. However, color is formed by the formation of a kinonic structure.

Example:



Pyrocatechol

CARBOXYL GROUP

The solubility group of the compounds containing the carboxyl group is 4. These compounds show acidity. Although some phenols, nitrophenols and primary sulfonamides are acidic, the solubility groups are 5. That is, they are not soluble in 5% sodium bicarbonate although they dissolve in 5% sodium hydroxide. The search for the carboxyl group is similar to that of the ester group. However, it is necessary to esterify the carboxyl group before.

Ferri Hydroxamate Test: Two part (2K) anhydrous ethyl alcohol and one part (1K) sulfuric acid are added to one part of (1K) substance. It is heated for 2 minutes. It is cooled and basified with sodium hydroxide solution. A mixture of 0.5 N hydroxylamine hydrochloride solution and 5% iron-3-chloride solution in 95% ethanol is added to the mixture. Purple-red-magenta color indicates the presence of carboxyl groups.

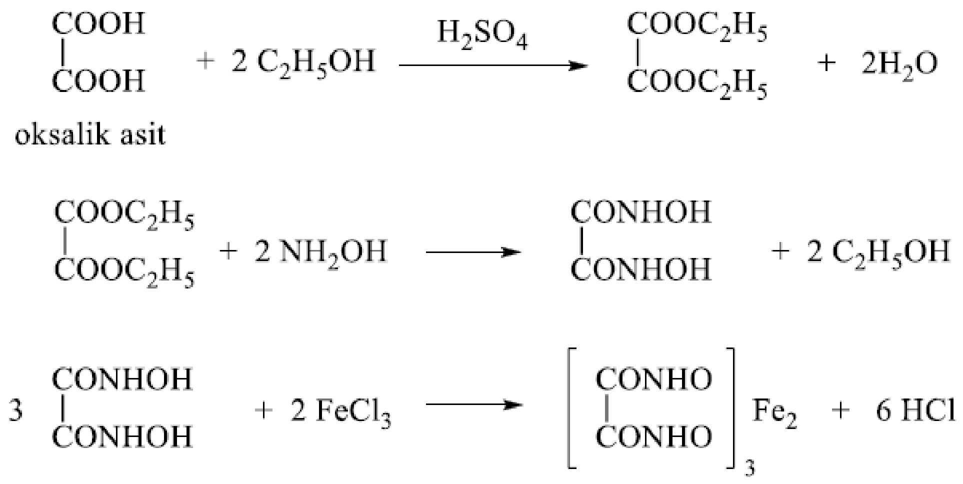
$$RCOOH + C_2H_5OH \xrightarrow{H_2SO_4} RCOOC_2H_5 + H_2O$$

$$RCOOC_2H_5 + NH_2OH \longrightarrow RCONHOH + C_2H_5OH$$

$$3\ RCONHOH + FeCl_3 \longrightarrow (RCONHO)_3Fe + 3\ HCl$$

Colored compound

Example:



$$\begin{array}{l} COOH \\ | \\ COOH \end{array} + 2\ C_2H_5OH \xrightarrow{H_2SO_4} \begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} + 2H_2O$$

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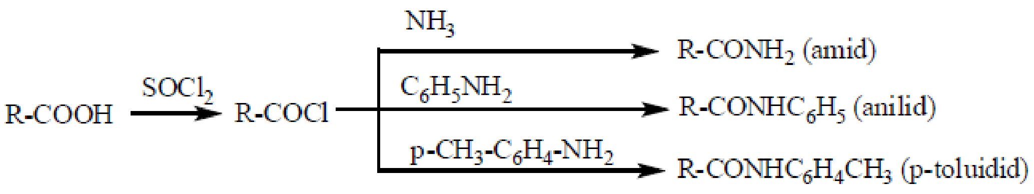
$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} + 2\ NH_2OH \longrightarrow \begin{array}{l} CONHOH \\ | \\ CONHOH \end{array} + 2\ C_2H_5OH$$

$$3 \begin{array}{l} CONHOH \\ | \\ CONHOH \end{array} + 2\ FeCl_3 \longrightarrow \left[\begin{array}{l} CONHO \\ | \\ CONHO \end{array} \right]_3 Fe_2 + 6\ HCl$$

Colored compound

Formation of Amide, Anilide and Toluidide: Carboxylic acid is treated with ammonia, aniline or p-toluidine after being converted into acid chloride; the resulting solid is filtered off. After crystallization from water or aqueous ethanol, the melting point is checked.

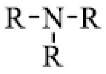


AMINE GROUP

It is divided into two groups as aliphatic and aromatic. They may also be primary, secondary or tertiary.

Primary aliphatic amine: $R-NH_2$

Secondary aliphatic amine: $R-NH-R$

Tertiary aliphatic amine: 

$$\underset{\displaystyle R}{R-\overset{}{N}-R}$$

Searching for Primary Amine Group (Primary Amine Group Test)

Rimini Test: It is an experiment for aliphatic amines. Some compound is dissolved in acetone. When 2 to 3 drops of sodium nitroprussite solution are added, the aliphatic amine group gives a purple-red color.

Isonitrile Test: Applied for primary aliphatic and aromatic amines. A sample is mixed with 2 drops of chloroform and 1 ml of 2 N NaOH solution and heated slightly. In the meantime, a very stenchy odor is produced by the formation of very smelly alkyl isonitrile. As primary aromatic amines respond positively to this experiment, other experiments should be done and decided.

$$R\text{-}NH_2 + CHCl_3 + 3\,KOH \longrightarrow R{-}N{\equiv}C + 3\,KCl + H_2O$$

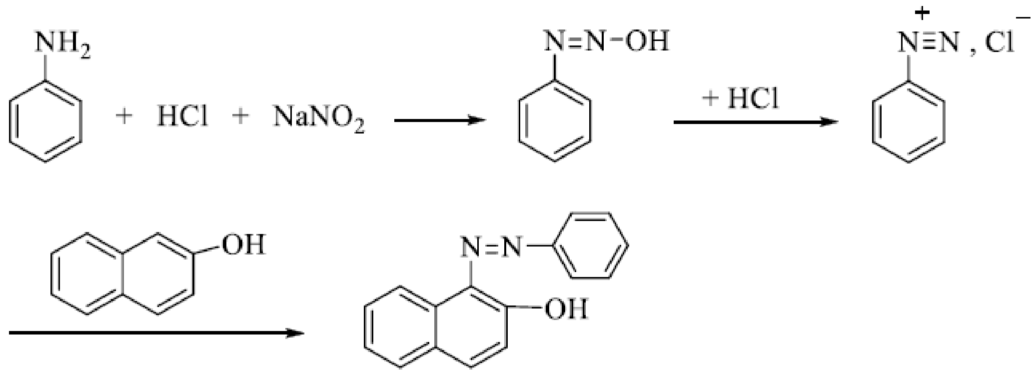
Lignin Test: A few samples are dissolved in a few drops of alcohol, heated and dripped on a piece of newsprint while hot. On cooling, 2 drops of 6 N HCl solution are added dropwise. The yellow or orange color indicates that it is positive.

Primary Aromatic Amine Group Test

The presence of this group is searched by the diazotization reaction. During the test, the tubes must be cooled in an ice bath or in a running tap water, and the temperature should be kept at a maximum of 4 ° C.

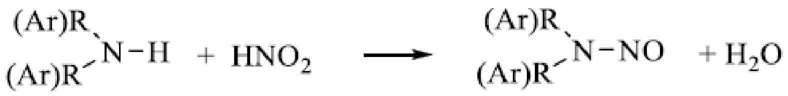
<u>Diazo Test:</u> A quantity of substance is dissolved in 10% hydrochloric acid in a test tube. A 10% sodium nitrite solution is added to the second tube. In a third tube, 10% sodium hydroxide solution and 10% β-naphthol solution are added. First, the tubes containing sodium nitrite and sample hydrochloric acid solution are mixed dropwise and stirred continuously.

Afterwards, the β-naphthol solution is added again by shaking dropwise. A red color or precipitate indicates the presence of the primary aromatic amine. Black or yellow colored precipitate indicates negative.



Searching for a Secondary Amine Group (Secondary Amine Group Test)

<u>Liebermann Test:</u> N-nitrosamines, which are produced by nitric acid of aliphatic and aromatic secondary amines, give a Liebermann reaction with a few exceptions.



$$\mathrm{(Ar)R,(Ar)R{-}N{-}H + HNO_2 \longrightarrow (Ar)R,(Ar)R{-}N{-}NO + H_2O}$$

After nitrosamine formed according to the above equation, after being separated from the acid solution with ether and evaporating the ether, 20-30 mg of the residue obtained is treated with a quantity of phenol and a few ml of concentrated sulfuric acid, slightly heated, cooled and poured into water.

If there is nitrosamine, a red color will occur, and by the addition of alkaline the color will turn blue.

Searching for a Tertiary Amine Group (Tertiary Amine Group Test)

<u>Conversion to quaternary ammonium salts:</u> Tertiary amines form quaternary ammonium salts in treatment with alkyl iodides. For this, the tertiary amine and the alkyl iodide (usually methyl iodide) are reacted either directly or after being dissolved in a suitable solvent. Diagnosis is made by finding the melting point of the quaternary ammonium salt formed (by comparison with the known one).

$$R_3N + CH_3I \longrightarrow [\ R_3NCH_3\ ]^{+} I^{-}$$

Separation of Primary, Secondary and Tertiary Amines (Hinsberg Test or Reaction)

If the mixture of primary, secondary and tertiary amines is treated with benzene or p toluenesulfonyl chloride (CH3-C6H4-SO2Cl) in an alkaline environment, the following results are obtained:

The sulfonamides formed by the primary amines are soluble in alkali hydroxide; sulfonamides derived from secondary amines are insoluble in alkali hydroxide; tertiary amines do not react with benzene sulfonyl chloride or p-toluene sulfonyl chloride.

$$\text{R-NH}_2 + \text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{Cl} + \text{NaOH} \longrightarrow [\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{NR}]^- \ \text{Na}^+$$

(suda çözünür)

$$\text{R}_2\text{N} + \text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{Cl} + \text{NaOH} \longrightarrow \text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{NR}_2$$

(NaOH'de çözünmez)

$$\text{R}_3\text{N} + \text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{Cl} + \text{NaOH} \longrightarrow \text{Reaksiyon yürümez}$$

MELTING POINT DETERMINATION

The melting point of the solids is specific and the unknown compounds can be determined by after the determination of the functional groups and melting point. Melting point determination is generally made in heat-resistant and pistol-shaped pyrex tubes. Paraffin, liquid vaseline, silicon or sulfuric acid may be used. However, sulfuric acid is not preferred because of the possibility that the tube can be broken during heating and thus various accidents may occur. The reason for the use of these liquids is that they are homogenously heated.

Even if the tube is heated from only one point, the temperature of these liquids is the same all over. Whereas if this heat is applied to water, the other parts of the water are not at the same temperature. Vaseline will be used in laboratory studies. The melting point is determined in thin capillary tubes. The reason for the use of capillary tubes is that the material of the pipe is very thin. Otherwise, when the material is filled into a thick pipe, the melting of the material will be a little later and will cause errors.

One side of the capillary tube must be completely closed. Otherwise, during the experiment, vaseline or the solvent enters the tube melt the substance. The capillary tube is immersed into the compound through the open end of the pipe to fill the sample into the pipe. Thus, solids are collected in the mouth of the capillary tube. The height of the substance in the tube is provided to be 5-6 mm. The capillary tube is then discharged through the normal pipe 8-10 times to ensure that the material is completely in place and no air gap is present. Otherwise, during the heating, the remaining air expands by warming up and pushes the solid upwards and the melting point is not fully determined. Liquid Vaseline is filled into the melting point determination tube. It is useful to completely fill the triangular part of the vaseline tube. Thus, during the heating, there will be a circulation in the triangle and the warming will be more homogenous. Immerse the thermometer in the liquid vaseline filled with the tube (300 ° C). The lower end of the thermometer is the continuation of the mouth of the tube and the center of the forming portion. The capillary and the lower ends of the thermometer must be aligned same position. The capillary tube is connected to the thermometer. White thread can be used as tying tool.

After all these processes are completed, the tube is heated from the bottom. The temperature of the thermometer does not increase proportionally with the temperature in the tube during rapid heating. The ideal heating is the one that increases by 3-4 ° C per minute. However, the best way to do this is to do the experiment twice because it will take a very long time. In the first, a coarse melting point is detected. In the second experiment, the heating is very slow in the vicinity of the first detection. The melting point is exactly determined. If the list of substances given as a sample is taken into consideration, the melting points of all substances are given at 2-3 ° C intervals. In the experiment, the starting and complete end points of the melt are determined.

Some substances do not melt at their melting points but decompose. These substances change color in this degree. The color turns yellow or brown. For such compounds, this point is given as a melting point in the list. Some substances decompose before they melt, ie they break down. For this reason, 25-30 ° is continued to be heated after the point where the color changes. If there is no change, the first point is considered to be the melting point. The melting point of the melting point is the end point of the liquid.

CAUTION: Do not pour vaselin into the sink after the melting point is determined. Put it in the bottle you bought it because it will be reused.

BOILING POINT DETERMINATION

This applies to liquids, boiling points will be determined instead of the melting point of the samples. Heat-resistant glass pyrex tube is thoroughly cleaned and dried for boiling point determination. Liquid is put into the tube and the thermometer will not touch the glass but the mercury is completely immersed in the liquid. The tube is then heated from the bottom. It is seen that the boiling point boils the liquid and there is no increase in the thermometer. This is the boiling point of the liquid sample.

CONCLUSION: After the melting or boiling point of the sample has been determined, the samples given below are found in the list. Compare the physical properties, elemental analysis, and the functional groups you find to determine which of these substances are your sample. Then apply specific reactions of the substance you suspect and find out which is the substance.