C-142 (Expt. No. 1)

Element Detection and Characterization of Organic Compounds

*An organic substance (**O. S**) supplied to you may be a solid or liquid. The solid specimen may be in flakes, amorphous powder, or crystalline. It should be reduced to fine particles by grinding using mortar and pestle before proceeding for any test. (**However avoid touching the compound**)*

1. Physical properties of a compound:

(a) Solid/ liquid (b) Colour, (b) structure – (crystalline or amorphous) (if it is a solid), (c) Odour (Do not inhale the compound directly) (d) Solubility (hot/ cold water) (e) acidic/basic/neutral

2. Chemical tests:

Heating on a copper foil:

A piece of copper foil is first to be heated in non luminous Bunsen flame to red hot condition and then cooled. Take a pinch of **O**. **S**. on the preheated copper foil (in cold condition). Heat it gently in the non luminous flame. Bring it out and cool to room temperature, Aromatic **O. S.** produce luminous flame with soot (unburnt C). Aliphatic or alicyclic substances produce luminous flame without much soot under red hot condition the flame will be colored green indicating the presence of halogen (***Beilstein test***)

Sodium Fusion: (Na – M. P.: 97.5^{o} C, B. P.: 880^{o} C)

To detect the presence of N, S, X (halogen) it is necessary to fuse **O**. **S**. with metallic sodium (***Lassaigne's Test)***: Place a piece of sodium metal (about a quarter size of a pea) in an ignition tube (a soft glass test tube) and a small amount of **O**. **S**. Hold the tube by a test tube holder and heat it gently and carefully (exposing the mouth of the tube away from you) on the Bunsen flame when solid melts. The tube has to be shaken carefully in the flame to avoid excessive local heating and to ensure mixing of the sample with the melted sodium. (It may be temporarily drawn out of the flame in the case of violent action), Then heat slowly then prolong heating to red hot condition. Then immediately immerse the tube in 5 – 10 ml distilled water taken in a porcelain dish / mortar. Filter the whole lot to a boiling test tube and boil the solution carefully and gently for five minutes, filter in cold condition and collect the

filtrate. This solution is called *Sodium Fusion Extract*. The filtrate should be water-clear and alkaline. If it is dark colored the whole fusion operation is to be repeated.
(Take the O.S. as minimum as possible of to get a water-clear solution)

(a) Nitrogen: To a potion of the filtrate add 0.2 g of powdered ferrous sulphate crystals and heat the mixture gently till it starts boiling. Sufficient dilute sulfuric acid is added to the mixture to dissolve the iron(III)/iron(II) hydroxide formed and to make the solution acidic. A **Prussian blue precipitate or coloration** indicates the presence of nitrogen. Occasionally, an indefinite greenish blue coloration also results in this test. In such a case the fusion test has to be repeated using a mixture of the unknown **O. S.** and pure glucose. If sulfur is present in **O. S.**, a black precipitate FeS will be produced on adding ferrous sulphate. However it is not usually necessary to remove FeS by filtration before proceeding for the test of nitrogen.

(b) Sulfur: To another portion of the filtrate add a few drops of a freshly prepared dilute solution of sodium nitroprusside ($Na_2[Fe(CN)_5NO]$). An intense **pink coloration indicates the presence of sulfur**.

(i) Sulfur, Nitrogen present: When both these elements are present, fusion results in the formation of sodium sulfocyanide (Na^+ CNS^-). The sodium carbonate extract may not respond to the Prussian blue test. In such case proceed as follows. Acidify 1 cc of sodium fusion extract with dil. HCl and add 1-2 drops of $FeCl_3$ solution, a **blood red coloration** will indicate the presence of **sulfur and nitrogen**.

(c) Halogens: Nitrogen and sulfur may interfere with the test for halogen. Thus, two different procedures are there for testing the presence of halogens.

(i) **Nitrogen and sulfur absent:** A portion of the filtrate is acidified with dil. HNO_3 an aqueous $AgNO_3$ solution is added. A precipitate of silver halide (curdy white for Cl, pale yellow for Br and yellow for I) indicates the presence of chlorine, bromine and iodine in the O. S. If only one halogen is present, it may be identified by decanting the mother liquor, washing the precipitate with distilled water and treating the precipitate with dilute. aqueous ammonia.

If the precipitate is white and dissolves readily in dilute NH_3 and reappears on acidification of the solution with dilute. HNO_3 – Chlorine is indicated.

If the precipitate is pale yellow and dissolves in dilute NH_3 with difficulty but readily in liquor ammonia and reappears on acidification with dilute HNO_3 - bromine is indicated.

If the precipitate is yellow and not soluble in liquor NH_3 – iodine is indicated.

(ii) **Nitrogen and Sulfur present**: The tests of halogens have to be modified as follows if nitrogen and sulphur are present.

A portion of the filtrate is rendered acidic with dilute HNO_3 and the solution is evaporated to half its original volume to expel HCN or H_2S. The residual solution is then diluted with an equal volume of distilled water and then used for performing the tests of halogens as described above.

By element detection, it is possible to judge to which category the O. S. belongs.

Test for functional group:

Note: ***Decide the category of your O.S. based on the element present. For example, in case of have N in your O.S., you have to test for nitrogen containing functional group as well as C, H and O containing groups.***

C, H and O containing groups: The possible functional groups are

(a) -COOH , (b) Ar-OH (Acidic groups) (c) –CHO and (d) Keto group

(There are more functional groups but only these will be given to you)

(a) **Test for carboxyl group:** To .1g of compound solution add some saturated $NaHCO_3$ solution to it. Effervescences take place with the release of CO_2. **Carboxylic acid confirmed**. (However, substituted phenols such as nitrophenols, aldehydrophenols, and polyhalophenols are sufficiently acidic to give this test with less vigorous effervescences)

(b) **Test for Phenol: (Test with neutral $FeCl_3$)** To a small amount of O.S. solution 2 drops of neutral $FeCl_3$ is added. **A blue, green, red or violet colour** indicates presence of **phenolic group**.

(c) **Carbonyl compound:** Forms 2,4 dintrophenyl hydrazones (bright orange yellow solids) in acidic medium. To a small amount of O.S. solution add 2-3 drops of 2,4 dintrophenylhydrizine. If a bright orange yellow solids (2,4-dintrophenyl hydrazones) separates out, the compounds contains a carbonyl group. (If precipitates don't form, heat the mixture gently and keep for 5-10 minutes to see the result.)

(i) Test for aldehyde: (Tollen's Test) Add a few drops of O. S. (~0.2g) to Tollen's reagent and keep the test tube in a water bath without disturbing. A silver mirror is formed on the side of the test tube. **Aldehyde confirmed**.

(ii) If the above test does not give any result the O.S. contains a keto group.

C, H, N containing O.S.: Possible groups are:

(a) $-NO_2$ and (b) $-NH_2$

(a) **Test for NO_2: Mulliken-Barker test:** Take 0.2 gm or 2- 3 drops of OS in a test tube, add 4-5 ml of alcohol, a pinch of zinc dust and 10% $CaCl_2$, boil the mixture for 2-3 minutes. Filter the solution in to a test tubes containing Tollen's reagent. A white precipitate turning grew on standing indicates nitro group. (Mostly you see the grey precipitates as a result of excess of the filtrate).

(b) **Test for $-NH_2$ (Azo dye test):** Take 0.2g of the O.S. in dil. HCl and cool in an ice bath. To this solution add cold solution of about 2.5% $NaNO_2$. Add this solution to an alkaline solution of β-naphthanol soln. Formation of a yellow-orange dye indicates the presence of $-NH_2$.