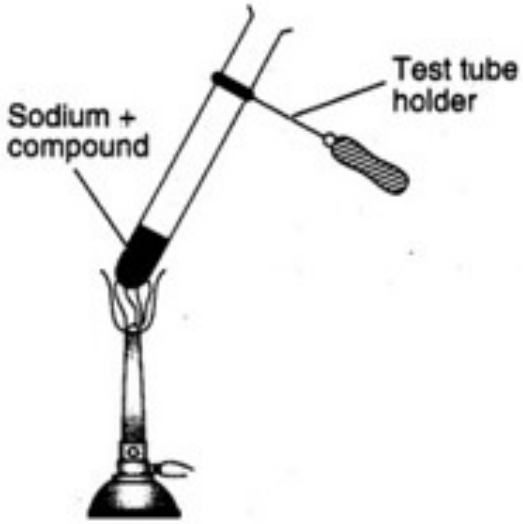
SEM-IV (Hons)

PRACTICAL

Qualitative Analysis of a Single Solid Organic Compound

Dr. Samiran Mondal, MRSC
Assistant Professor
Rammohan College, Kolkata



(1) Heat sodium and substance till all fumes cease to be evolved.

(2) Plunge ignition tube in 10–15 ml distilled water.

(3) Boil the contents for five minutes.

(4) Filter the extract while still hot.

Lassaigne's test is used for the detection of elements: Nitrogen (N), Sulfur (S), Chlorine (Cl), Bromine (Br) and Iodine (I). This test involves following two steps.

i) preparation of sodium fusion extract (SFE).

ii) Detection of elements using SFE.

i) Preparation of SFE

A small amount of organic substance is fused with a small quantity of sodium metal in a fusion tube. The red hot fusion tube is then plunged into distilled water and the contents are boiled for a few minutes, then cooled and filtered. then cooled and filtered.

The filtrate obtained is called sodium fusion extract (SFE) or Lassaigne's extract. It is usually alkaline. If it is not alkaline, a few drops of NaOH solution may be added to make it alkaline.

Question: Why is sodium fusion extract alkaline?

Answer: The excess of sodium reacts with water to furnsish hydroxide ions along with the liberation of dihydrogen gas.

ii) Detection of elements using SFE

Thus obtained SFE is used to detect the presence of elements like N,S,Cl, Br & I.

The elements in the organic compound react with sodium during fusion reaction as follows:

$Na + C + N \longrightarrow NaCN$ (if N is present)

$2Na + S \longrightarrow Na_2S$ (if S is present)

$Na + S + C + N \longrightarrow NaSCN$ (if both N & S are present & insufficient amount of Na is used)

$Na + X \longrightarrow NaX$ (If halogens are present)

Where

X = Cl/Br/I

Hence SFE may contain any of or all of ionic forms of respective elements.

Detection of Nitrogen

To a portion of SFE, freshly prepared ferrous sulphate, $FeSO_4$ solution is added and warmed. Then about 2 to 3 drops of $FeCl_3$ solution are added and acidified with conc. HCl. The appearance of a Prussian blue color indicates the presence of nitrogen.

$$FeSO_4 + NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$

$$6NaCN + Fe(OH)_2 \longrightarrow Na_4[Fe(CN)_6]$$

sodium ferrocyanide

$$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12\ NaCl$$

Ferric ferro cyanide
(Prussian blue)

Note:

1) In Lassaigne's test, afresh solution of fresh solution of $FeSO_4$ must be used. Otherwise, it is oxidized to ferric sulfate due to aerial oxidation.

2) HCl is added to convert Ferrous hydroxide, a green precipitate to ferrous chloride, which is soluble in water. Otherwise the green precipitate may interfere with Prussian blue color.

$Fe(OH)_2 + 2HCl$ ----------> $FeCl_2 + 2H_2O$

When both N & S are present:

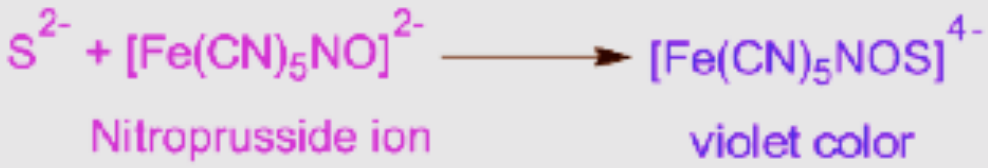
However if both N & S are present in the organic compound and SFE is prepared with insufficient amount of Na metal, the thiocyanate (SCN^-) is formed instead of cyanide ion (CN^-). The thiocyanate, SCN^- reacts with Fe^{3+} to give a blood red coloration due to formation of $[Fe(SCN)]^{2+}$.

$Fe^{3+} + SCN^-$ ----------> $[Fe(SCN)]^{2+}$

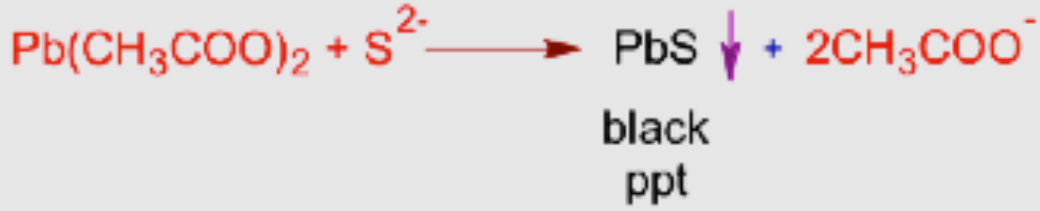
Note: However, if sodium fusion is carried out with excess of sodium, the thiocyanate, SCN^- is decomposed to give CN^- & S^{2-}. Hence in this case, sulfur and nitrogen are to be identified in separate tests.

Detection of Sulfur

i) The appearance of a **deep violet color** upon addition of a few drops of sodium nitroprusside to sodium fusion extract (SFE) indicates the presence of sulfur.



ii) Sulphur can also be detected by adding lead acetate to SFE, acidified with acetic acid. The formation of a **black precipitate (PbS)** indicates the presence of sulfur.



Detection of Halogens

The sodium fusion extract, SFE can be used to detect the presence of chlorine, bromine and iodine but not fluorine. To detect their presence, the SFE is first acidified with HNO_3 and then added with $AgNO_3$ solution.

i) The formation of a curdy white precipitate that is soluble in NH_4OH indicates the presence of chlorine in the organic compound.

$$Cl^- + AgNO_3 \longrightarrow \underset{\text{white ppt.}}{AgCl\downarrow} + NO_3^-$$

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{soluble complex}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

ii) The formation of a **pale yellow** precipitate that is partially soluble in NH_4OH confirms the presence of bromine.

$$Br^- + AgNO_3 \longrightarrow \underset{\text{pale yellow ppt.}}{AgBr\downarrow} + NO_3^-$$

iii) Where as the formation of a **yellow** precipitate insoluble in NH_4OH confirms the presence of iodine in the organic compound.

$$I^- + AgNO_3 \longrightarrow \underset{\text{yellow ppt.}}{AgI\downarrow} + NO_3^-$$

Note:

1) It is not possible to detect the presence of fluorine since the solubility of AgF is more and thus no precipitate is formed.

2) If nitrogen or sulfur are present in the organic compound, the formation of black precipitates of AgCN or AgS may interfere during the test for halogens. Hence the CN^- and S^{2-} have to be removed from the SFE. This is done by boiling the SFE with conc. HNO_3 or glacial acetic acid to almost dryness. The CN^- and S^{2-} ions are removed as HCN and H_2S gases.

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN$$

$$Na_2S + HNO_3 \longrightarrow NaNO_3 + H_2S$$

SUMMARY

Test	Observation	Inference
SFE + $FeSO_4$ + $FeCl_3$ + HCl	i) A prussian blue color is formed. ii) Blood red coloration is observed.	i) Nitrogen is confirmed. ii) Both nitrogen and sulfur are confirmed.
i) SFE + Sodium nitroprusside ii) SFE + CH_3COOH + $Pb(CH_3COO)_2$	i) A violet coloration is observed. ii) A black precipitate is formed.	Sulfur is confirmed.
SFE + HNO_3 + $AgNO_3$	i) A white ppt. soluble in NH_4OH is formed. ii) A pale yellow ppt. partially soluble in NH_4OH is formed. iii) A yellow ppt. insoluble in NH_4OH is formed.	i) Chlorine is confirmed. ii) Bromine is confirmed. iii) Iodine is confirmed.