Detection of Elements in Organic Compounds

Detection of elements present in an organic compound constitutes an important step in its analysis. All the organic compounds contain carbon. Hydrogen is also present in most of the organic compounds (the few exceptions are the compounds such as CCl_4, CS_2, etc.). In addition to carbon and hydrogen other elements which are generally present in organic compounds are oxygen, nitrogen, sulphur and halogens.

Since nearly all the organic compounds contain carbon as well as hydrogen it is usually not necessary to carry out tests to detect them and their presence can be assumed without testing for them. Here, we shall study the tests for the detection of nitrogen, sulphur and halogens only.

Detection of Nitrogen, Sulphur, Chlorine, Bromine and Iodine by Lassaigne's Test

This is the most dependable test for the detection of nitrogen, sulphur and halogens. This test is also known as sodium fusion test. In order to perform this test, first of all sodium extract or Lassaigne's extract is prepared as described below :

Preparation Of Lassaigne's Extract

Take a small piece of dry sodium in a fusion tube. Heat the tube slightly so that it melts to a shining globule. Add a pinch of the organic compound. Heat it slowly to start with so that the compound reacts with sodium metal. Now heat it strongly. Plunge the red hot tube into a china dish containing distilled water. Crush the contents with a glass rod and heat to boiling. Remove the insoluble matter by filtration. The filtrate is called Lassaigne's extract.
Nitrogen, sulphur and halogens present in an organic compound are detected by making use of Lassaigne's extract.

Detection Of Nitrogen

To a small portion of Lassaigne's extract (usually alkaline), add 2 ml of freshly prepared ferrous sulphate solution and heat. Now add to it 2-3 drops of ferric chloride solution and acidify with cone, hydrochloric acid. A prussian blue colouration indicates the presence of nitrogen in the compound.

Chemistry of the test

If nitrogen is present in the compound, the sodium extract would contain sodium cyanide formed during fusion. On adding the required reagents, sodium cyanide reacts to form ferric-ferrocyanide which has prussian blue colour.

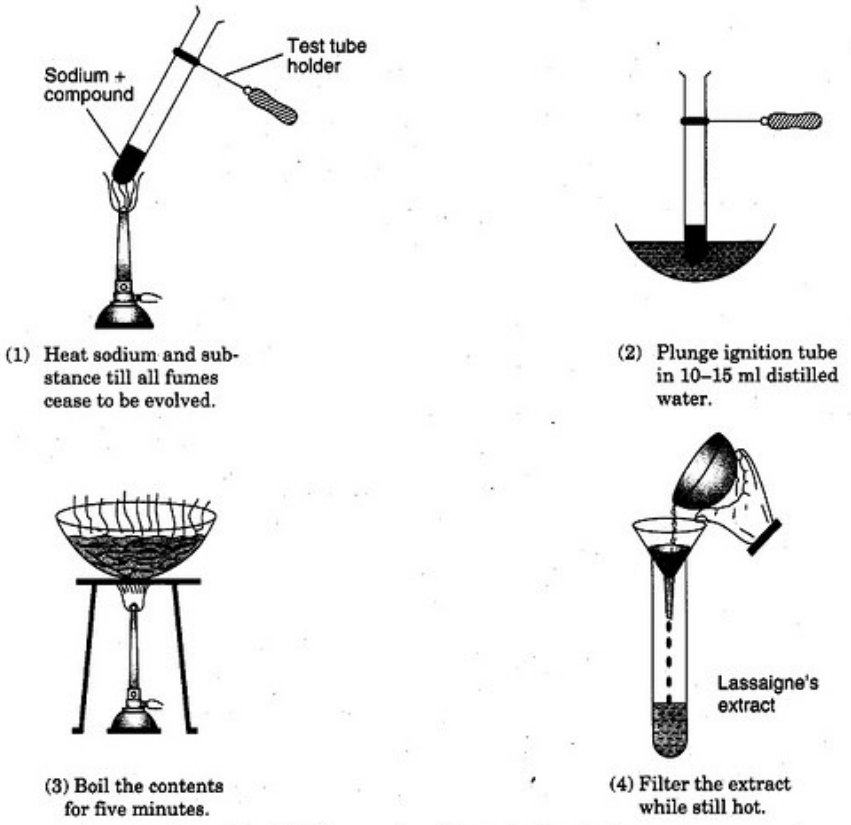
$$Na + \underbrace{C + N}_{\text{(From organic compound)}} \xrightarrow{\text{Fuse}} NaCN$$

$$FeSO_4 + 2NaOH \longrightarrow \underset{\text{Green ppt.}}{Fe(OH)_2\downarrow} + Na_2SO_4$$

$$Fe(OH)_2 + \underset{\substack{\text{(From}\\ \text{sodium}\\ \text{extract)}}}{2NaCN} \longrightarrow Fe(CN)_2 + 2NaOH$$

$$Fe(CN)_2 + 4NaCN \longrightarrow \underset{\text{Sod. ferrocyanide}}{Na_4[Fe(CN)_6]}$$

$$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\substack{\text{Ferric ferrocyanide}\\ \text{(prussian blue colour)}}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$



(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.

Fig. 10.1. Preparation of Lassaigne's extract.

The purpose of acidifying the reaction mixture in the end is to dissolve any green ppt. of $Fe(OH)_2$ since it may lead to wrong inferences.

Nitrogen and sulphur present together. If the organic compound contains both nitrogen and sulphur, sodium sulphocyanide (NaCNS) is formed during preparation of Lassaigne's extract. Sodium sulphocyanide reacts with ferric chloride and gives blood red colouration due to formation of ferric sulphocyanide.

$$Na + \underbrace{C + N + S}_{\text{From organic compound}} \longrightarrow NaCNS$$

$$3NaCNS + FeCl_3 \longrightarrow \underset{\substack{\text{Blood red}\\ \text{colouration}}}{Fe(CNS)_3} + 3NaCl$$

Thus, appearance of a blood red colouration on performing Lassaigne's test for nitrogen indicates the presence of both nitrogen and sulphur in the organic compound.

Detection Of Sulphur

1. Sodium nitroprusside test. To a small portion of Lassaigne's extract add a few drops of sodium nitroprusside solution. A purple colouration indicates the presence of sul¬phur in the compound.

Chemistry of the test

During preparation of Lassaigne's extract sulphur from the organic compound combines with sodium to form sodium sulphide. Sulphides give purple colouration on reaction with sodium nitroprusside.

$$2Na + \underset{\text{(From organic compound)}}{S} \xrightarrow{\text{Fuse}} Na_2S$$

$$\underset{\text{(From sodium extract)}}{Na_2S} + \underset{\text{Sod. nitroprusside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{Purple colouration}}{Na_4[Fe(CN)_5NOS]}$$

2. Lead acetate test. Acidify a small portion of Lassaigne's extract with acetic acid and add a few drops of lead acetate solution. The formation of black ppt. indicates the presence of sulphur in the compound.

Chemistry of the test

$$Na_2S + (CH_3COO)_2\ Pb \longrightarrow \underset{\text{Black ppt.}}{PbS\downarrow} + 2CH_3COONa$$

Detection Of Chlorine, Bromine And Iodine

1. Silver nitrate test. To a small portion about 2 ml of Lassaigne's extract add 1 ml of cone, nitric acid and boil for some time. Cool the contents and add to it silver nitrate solution.
(a) **White precipitate, soluble in ammonium hydroxide**, indicates the presence of chlorine in the organic compound.
(b) **Pale yellow precipitate, sparingly soluble in ammonium hydroxide**, indicates the presence of bromine in the compound.
(c) **Yellow precipitate, insoluble in ammonium hydroxide**, indicates the presence of iodine in the organic compound.

Chemistry of the test

(a) For Chlorine

$$Na + Cl \xrightarrow{Heat} NaCl$$
(From org. compound)

$$NaCl + AgNO_3 \longrightarrow AgCl\downarrow + NaNO_3$$
Silver chloride (White ppt.)

$$AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2H_2O$$
(Soluble)

(b) For Bromine

$$Na + Br \xrightarrow{Heat} NaBr$$
(From org. compound)

$$NaBr + AgNO_3 \longrightarrow AgBr\downarrow + NaNO_3$$
Silver bromide (Pale yellow ppt.)

(c) For Iodine

$$Na + I \xrightarrow{Heat} NaI$$
(From org. compound)

$$NaI + AgNO_3 \longrightarrow AgI\downarrow + NaNO_3$$
Silver iodide (Yellow ppt.)

The function of adding cone. HNO3 and boiling is to decompose any sodium cyanide or sodium sulphide present in the extract. Otherwise these compounds will interfere with the tests of halides since NaCN gives a white ppt. with silver nitrate while Na_2S gives a black ppt.

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN\uparrow$$
$$Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S\uparrow$$

2. Carbon disulphide test. Acidify a small portion of Lassaigne's extract with dil. HCl and add a few drops of carbon disulphide (or CCl_4 or $CHCl_3$). Now add freshly prepared chlorine water and shake vigorously.

(a) Appearance of **orange colour** in the carbon disulphide layer indicates the presence of **bromine**.

(b) Appearance of **violet colour** in the carbon disulphide layer indicates the presence of **iodine**.

Chemistry of the test

Chlorine can displace bromine and iodine from their respective halides in solution. Bromine or iodine thus liberated can turn the carbon disulphide layer orange or violet.

$$Cl_2 + \underset{\text{(From sodium extract)}}{2NaBr} \longrightarrow Br_2 + 2NaCl$$

$$Cl_2 + \underset{\text{(From sodium extract)}}{2NaI} \longrightarrow I_2 + 2NaCl$$

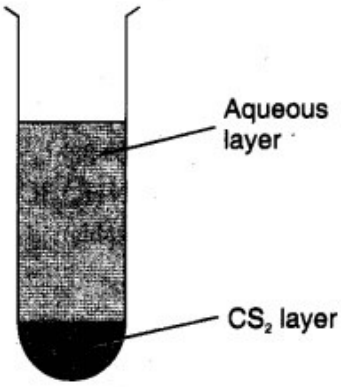


Fig. 10.2. Carbon disulphide test.

Table 10.1. Detection of N, S, Cl, Br and I by Lassaigne's Test

Experiment	Observations	Inference
Preparation of Lassaigne's extract Fuse a small piece of sodium in a fusion tube. Add a little organic compound to it and heat. Plunge it in a china dish containing distilled water. Boil the contents and filter. The filtrate is called Lassaigne's extract.		
1. Test for Nitrogen: To 2 ml of Lassaigne's extract add 2 ml of freshly prepared $FeSO_4$, boil and add a few drops of $FeCl_3$ solution and concentrated hydrochloric acid.	Prussian blue colour	Nitrogen present
2. Test for Sulphur : (a) To 2 ml of Lassaigne's extract add 2-3 drops of acetic acid and 1 ml of **lead acetate solution**.	Black ppt.	Sulphur present
(b) To 2 ml of Lassaigne's extract add a few drops of **sodium nitroprusside solution**.	Purple colour	Sulphur present

3. Test for Halogens : **(a) Silver nitrate test** Acidify a little of Lassaigne's extract with concentrated HNO_3 boil, cooled and add silver nitrate solution.	(i) **A curdy white ppt.** soluble in excess of NH_4OH. (ii) **A pale yellow ppt.** sparingly soluble in NH_4OH. (iii) **A bright yellow ppt.** insoluble in NH_4OH.	Chlorine present Bromine present Iodine present
(b) Carbon disulphide test Acidify another portion of Lassaigne's extract with dil. HCl and add 1 ml of CS_2 and two drops of chlorine water and shake.	(i) **Orange colour** in CS_2 layer. (ii) **Violet colour** in CS_2 layer.	Bromine present Iodine present