🎯 **Learning outcomes**
By the end of this chapter, Students should be able to:

Detect N, S, and halogens in organic compounds by Lassaigne's test.

13.2 Qualitative analysis of organic compounds (detection of N, S, and halogens by Lassaigne's test)

Detection of foreign elements

As we know, ***hydrocarbons and their derivatives*** are called ***organic compounds***. It means carbon and hydrogen are the essential elements in organic compounds. Many organic compounds include oxygen as well. Besides, a few elements like nitrogen, sulphur, halogens, phosphorus, etc., may be present in organic compounds. These elements are called **foreign elements**.

Generally, foreign elements are detected via the formation of sodium extract, also called Lassaigne's extract. The whole process is called the sodium extract or Lassaigne's extract test. This is done because organic compounds are covalent compounds. Reactions involving covalent bonds are slow and complex. It is difficult to test for the presence of foreign elements as such. So, these are first changed into ionic form by strongly heating them with reactive sodium metal, whose presence could be easily tested.

Preparation of Sodium extract or Lassaigne's extract:

Sodium metal is generally stored in kerosene. A small piece of sodium metal is taken and dried in the fold of blotting paper. Then it is kept in a fusion tube or ignition tube and heated gently so that the sodium metal just melts into a shiny globule. Then, after cooling it slightly, the sample of the organic compound, in which the presence of foreign elements is to be detected, is added in an amount nearly equal to the size of sodium. Then it is heated, first gently, then strongly, until red-hot and plunged into a porcelain basin containing water. The fusion tube and contents are crushed and warmed, then filtered. The filtrate is called sodium extract or Lassaigne's extract, and it is used to detect foreign elements.

The sodium extract is generally alkaline due to the presence of NaOH formed by the reaction of water with excess sodium.

$$H_2O + Na \longrightarrow NaOH + H_2 + heat$$

The following reactions occur during the preparation of Sodium extract if N, S, both N and S, or halogens are present in the organic compound, respectively.

$$Na + C + N \longrightarrow NaCN$$
Sodium cyanide

$$Na + S \longrightarrow Na_2S$$
Sodium sulphide

$$Na + C + N + S \longrightarrow NaCNS$$
Sodium thiocyanide

$$Na + X \longrightarrow NaX$$
Sodium halide

(where X= halogen i.e. Cl, Br, I etc)

1. Detection of Nitrogen

For the detection of nitrogen, the sodium extract must be alkaline. If it is not, it should be made alkaline by adding a small amount of NaOH solution. About 1 ml of the sodium extract is taken in a test tube, and a few drops of freshly prepared $FeSO_4$ solution are added. Then it is boiled, where dirty green ppt. is generally formed. After cooling in tap water, a few drops of $FeCl_3$ are added and acidified with dilute HCl. The formation of **Prussian blue** or **green** colouration indicates the presence of nitrogen in the given organic compound. The following reactions are involved.

$$Na + C + N \longrightarrow NaCN$$

$$2\,NaOH + FeSO_4 \longrightarrow Na_2SO_4 + Fe(OH)_2\downarrow$$
Dirty green ppt

$$Fe(OH)_2 + NaCN \longrightarrow Fe(CN)_2 + 2\,NaOH$$

$$Fe(CN)_2 + 4\,NaCN \longrightarrow Na_4[Fe(CN)_6]$$
Sodium ferrocyanide

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

Prussian blue or green coloured

During this test, the formation of blood red colouration indicates the presence of both nitrogen and sulphur in the organic compound. **(Test for both sulphur and nitrogen)**

$$Na + C + N + S \longrightarrow NaCNS$$
Sodium thiocyanide

$$3NaCNS + FeCl_3 \longrightarrow Fe(CNS)_3 + 3\,NaCl$$
Ferric thiocyanide
(blood red colored)

2. Detection of Sulphur:

The presence of sulphur is detected in two ways.

a) Lead acetate test: The sodium extract is acidified with acetic acid and then treated with lead acetate. The formation of **black ppt**. confirms the presence of sulphur.

$$Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH} 2\,CH_3COONa + PbS\downarrow$$
Lead acetate
Lead ethanoate

Sodium ethanoate (Sodium acetate)

black ppt

b) Sodium nitroprusside test: To a small portion of the sodium extract solution, nitroprusside solution is added. The appearance of **violet** colouration confirms the presence of sulphur in the organic compound.

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$$

Sodium nitroprusside — Sodium sulphonitroprusside

3. Detection of halogens

To detect halogens, the first 1 ml of the sodium extract is boiled with dilute nitric acid to remove cyanide or sulphide if present.

$$HNO_3(aq.) + NaCN\ (aq) \longrightarrow NaNO_3(aq.) + HCN\uparrow$$

$$HNO_3(aq.) + Na_2S\ (aq) \longrightarrow NaNO_3(aq.) + H_2S\uparrow$$

If not removed, these ions interfere with the result of the silver nitrate test as

$$AgNO_3 + NaCN \longrightarrow AgCN\downarrow + NaNO_3$$

white ppt

$$AgNO_3 + Na_2S \longrightarrow Ag_2S\downarrow + NaNO_3$$

black ppt

After boiling, it is cooled, and then a few drops of $AgNO_3$ solution are added. The formation of white ppt. soluble in ammonia solution (ammonium hydroxide) and reappearing in dilute HNO_3 indicates the presence of chlorine.

$$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + NaNO_3$$

white ppt

$$AgCl + 2\ NH_3(aq.) \longrightarrow [Ag(NH_3)_2]Cl$$

Diammine silver chloride
(soluble complex)

$$\text{Or, } AgCl + 2\ NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + H_2O$$

$$[Ag(NH_3)_2]Cl + 2\ HNO_3 \longrightarrow AgCl + 2\ NH_4NO_3$$

The formation of pale-yellow ppt. slightly soluble in ammonium hydroxide or aq. NH_3 indicates the presence of bromine.

$$AgNO_3 + NaBr \longrightarrow AgBr\downarrow + NaNO_3$$

pale yellow ppt

$$AgBr + 2\ NH_3(aq.) \longrightarrow [Ag(NH_3)_2]Br$$

Diammine silver bromide
(partially soluble)

The formation of **yellow ppt.** insoluble in ammonium hydroxide or NH_3 solution indicates the presence of iodine.

$$AgNO_3 + NaI \longrightarrow AgI\downarrow + NaNO_3$$

yellow ppt.

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