

Qualitative Analysis of Organic Compounds:

This is used to detect nitrogen, halogen and sulphur present in organic compound.

a) Sodium Extract: Aqueous solution containing soluble sodium salt of the elements *i.e* NaCl, Na₂S and NaCNS formed by fusion of compound with sodium metal.

b) Formation of Sodium Extract: It is a two-step process

Step 1: Organic compounds are fused with dry sodium in a fusion-tube

Step 2: Fused mass after extraction with water is boiled and filtered.

c) Use of Sodium Extract: Sodium extract (S.E.) is used to detect elements (other than C and H) and the tests are given in the table.

Element	Sodium Extract (S.E.)	Confirmed Test
Nitrogen	$\text{Na} + \text{C} + \text{N} + \Delta \rightarrow \text{NaCl}$	S.E. + FeSO ₄ + NaOH, boil and cool + FeCl ₃ + conc. HCl → Blue/ green colour Reactions Involved: $2\text{NaCN} + \text{FeSO}_4 \rightarrow \text{Fe}(\text{CN})_2 + \text{Na}_2\text{SO}_4$ $\text{Fe}(\text{CN})_2 + 4\text{NaCN} \rightarrow \text{Na}_4[\text{Fe}(\text{CN})_6]$ <p style="text-align: center;">Sodium Ferrocyanide</p> $3\text{Na}_4[\text{Fe}(\text{CN})_6] + 4\text{FeCl}_3 \xrightarrow{\text{HCl}} \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{NaCl}$ <p style="text-align: center;">Ferric Ferrocyanide Prussian Blue</p>
Sulphur	$2\text{Na} + \text{S} \rightarrow \text{Na}_2\text{S}$	(i) S.E. + sodium nitroprusside → Violet Colour (ii) S.E + CH ₃ CO ₂ H + (CH ₃ CO ₂) ₂ Pb → black ppt. Reactions Involved: (i) $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_3\text{NO}] \rightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$ <p style="text-align: center;">(Sodium Nitroprusside) (Violet Colour)</p> (ii) $\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}} \text{PbS} \downarrow + 2\text{CH}_3\text{COONa}$ <p style="text-align: center;">(Black ppt)</p>
Halogen	$\text{Na} + \text{X} + \Delta \rightarrow \text{NaX}$ <p>(X = Cl, Br, I)</p>	S.E. + HNO ₃ + AgNO ₃ →

Observation	Inference
1. Substance is coloured	
i) Blue	Copper salt
ii) Dark green	Chromium salt
iii) Green	Salts of Fe(II), Ni, Cu or Cr
iv) Light yellow or brown	Salts of Fe(III)
v) Dark brown	PbO ₂ , Bi ₂ S ₃
vi) Light pink	Salts of Mn
vii) Pink	Salts of Co
viii) Red	HgO, HgI ₂ , Pb ₃ O ₄
ix) Orange red	Sb ₂ S ₃
2. Substance is deliquescent	CaCl ₂ , ZnCl ₂ , MgCl ₂ , MnCl ₂ , nitrites, nitrates
3. Substance is heavy	Salts of Pb, Hg and Ba
4. Substance is light	Carbonates of Bi, Mg, Al, Zn, Ca, Sr

2. Effect of Heating:

Observation	Inference
1. Substance melts	Salts of alkali metals and salts having water of crystallisation.
2. Substance decrepitates (crackling noise)	NaCl, KI, Pb(NO ₃) ₂ and Ba(NO ₃) ₂
3. Substance swells (due to loss of water of crystallisation)	Alums, borates and phosphates
4. The substance sublimes and the colour of sublimate is	
i) White	HgCl ₂ , Hg ₂ Cl ₂ , NH ₄ X, AlCl ₃ , As ₂ O ₃ , Sb ₂ O ₃
ii) Yellow	As ₂ S ₃ and HgI ₂ (turns red when rubbed with glass rod).
iii) Blue black and violet vapours	Iodides
5. A residue (generally oxide) is left and its colour is	
i) Yellow (hot) and white (cold)	ZnO
ii) Reddish brown (hot); yellow (cold)	PbO
iii) Black (hot); Red (cold)	HgO, Pb ₃ O ₄
iv) Black (hot); Red brown (cold)	Fe ₂ O ₃
6. Gas is evolved	
(A) Colourless and odourless	
i) O ₂ - rekindles a glowing splinter	Alkali nitrates (2KNO ₃ → 2KNO ₂ + O ₂)

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ii) CO ₂ - turns lime water milky	Carbonates and oxalates ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$)
iii) N ₂	Ammonium nitrite ($\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$)
(B) Colourless gas with odour	
i) NH ₃ - Turns red litmus blue and mercurous nitrate paper black	Ammonium salts ($(\text{NH}_4)_2\text{SO}_4 \rightarrow \text{NH}_4\text{HSO}_4 + \text{NH}_3$)
ii) SO ₂ - Smell of burning sulphur, turns acidified K ₂ Cr ₂ O ₇ paper green	Sulphites and thiosulphates $\text{CaSO}_3 \rightarrow \text{CaO} + \text{SO}_2$
iii) HCl - Pungent smell, white fumes with ammonia	Hydrated chlorides $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + 4\text{H}_2\text{O} + 2\text{HCl}$
iv) H ₂ S - smell of rotten eggs, turns lead acetate paper black	Sulphides $\text{Na}_2\text{S} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2\text{S}$
(C) Coloured gas	
i) NO ₂ - Brown, turns starch iodide paper blue	Nitrites and nitrates of heavy metals $2\text{Cu}(\text{NO}_3)_2 \rightarrow 2\text{CuO} + 4\text{NO}_2 + \text{O}_2$
ii) Br ₂ - Reddish brown	Bromides $2\text{CdBr}_2 + \text{O}_2 \rightarrow 2\text{CdO} + 2\text{Br}_2$
(A) Turns starch paper yellow	
(B) turns starch iodide paper blue	
iii) I ₂ - Violet, turns starch paper blue	Iodides $2\text{CdI}_2 + \text{O}_2 \rightarrow 2\text{CdO} + 2\text{I}_2$
iv) Cl ₂ - Greenish yellow	Chlorides $\text{CuCl}_2 + \text{H}_2\text{O} \rightarrow \text{CuO} + 2\text{HCl}$
(A) bleaches moist litmus paper	$\text{CuO} + 2\text{HCl} \rightarrow \text{Cu} + \text{H}_2\text{O} + \text{Cl}_2$
(B) bleaches indigo solution	
(C) turns starch iodide paper blue	

3. Flame test:

Metals	Colour
Li	crimson red
Na	golden yellow
K	Violet
Ca	Brick red
Sr	Crimson

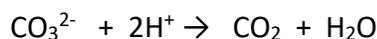
Ba

apple green

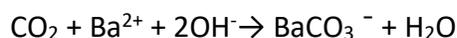
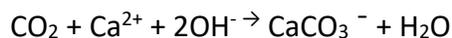
Test for Anions:

1. Carbonate (CO_3^{2-})

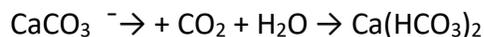
i) **Dilute HCl** : gives effervescence, due to the evolution of carbon dioxide.



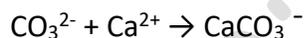
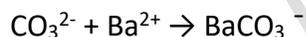
The gas gives turbidity with lime water and baryta water.



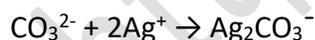
On prolonged passage of carbon dioxide in lime water, the turbidity slowly disappears due to the formation of soluble hydrogen carbonate.



ii) **Barium chloride or Calcium chloride solution**: White ppt of barium or calcium carbonate is obtained, which is soluble in mineral acid.



iii) **Silver nitrate solution**: White ppt of silver carbonate is obtained.

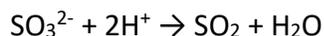


The ppt so obtained is soluble in nitric acid and in ammonia. The ppt becomes yellow or brown on addition of excess reagent and same may also happen if the mix is boiled, due to the formation of silver oxide



2. Sulphites (SO_3^{2-})

i) **Dilute HCl or Dilute H₂SO₄** : decomposes with the evolution of sulphur dioxide



The gas has a suffocating odour of burning sulphur.

ii) **Acidified potassium dichromate solution**: Turns filter paper moistened with acidified potassium dichromate solution, green due to the formation of Cr³⁺ ions.

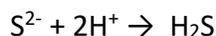
iii) **Lime water** : On passing the gas through lime water, a milky ppt is formed.

Precipitate dissolves on prolonged passage of the gas, due to the formation of hydrogen sulphite ions.

iv) **Barium chloride or Strontium chloride solution**: Gives white ppt. of barium or strontium sulphite.

3. Sulphide (S²⁻)

i) **Dil. HCl or Dil. H₂SO₄**: A colourless gas smelling of rotten eggs (H₂S) is evolved.

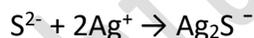


ii) The gas turns lead acetate paper black

iii) Gives yellow ppt. with CdCO₃



iv) **Silver nitrate solution**: black ppt. of silver sulphide insoluble in cold but soluble in hot dil nitric acid.



v) **Sodium nitroprusside solution** : Turns sodium nitroprusside solution purple

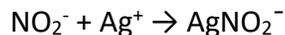


4. Nitrites (NO₂⁻)

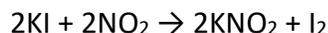
i) **Dil HCl and Dil. H₂SO₄** : Adding to solid nitrite in cold yields pale blue liquid (due to the presence of free nitrous acid HNO₂ or its anhydride N₂O₃) & the evolution of brown fumes of

nitrogen dioxide, the latter being largely produced by combination of nitric oxide with the oxygen of the air

ii) Silver nitrate solution : White crystalline ppt. is obtained



iii) Turns acidified KI - starch paper blue

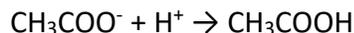


Starch + $\text{I}_2 \rightarrow$ Blue colour

iv) **Brown ring test:** When the nitrite solution is added carefully to a conc. solution of Iron(II) sulphate acidified with dil acetic acid or with dilute sulphuric acid, a brown ring is formed, due to the formation of $[\text{FeNO}]\text{SO}_4$ at the junction of the two liquids.

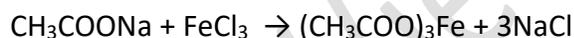
5. Acetate (CH_3COO^-)

i) **Dilute Sulphuric Acid :** Smell of vinegar is observed.



The following test is performed with the aqueous salt solution.

ii) **Iron (III) Chloride Solution:** Gives deep - red colouration

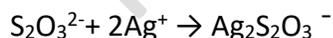


Brown colour

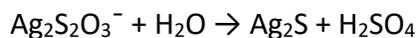
6. Thiosulphates

i) **Dil Hydrochloric acid:** Gives sulphur & sulphur di oxide

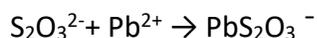
ii) **Silver nitrate solution:** Gives white ppt. of silver thiosulphate.



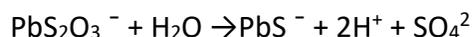
The ppt. is unstable, turning dark on standing, when silver sulphide is formed.



iii) **Lead acetate or Lead nitrate solution:** Gives white ppt.

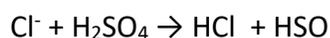


On boiling it turns black due to the formation of PbS.



7. Chloride (Cl⁻)

i) **Conc. H₂SO₄** : decomposes with the evolution of HCl.



Gas so produced

(1) Turns blue litmus paper red

(2) Gives white fumes of NH₄Cl when a glass rod moistened with ammonia solution is brought near the mouth of test tube.

ii) **Silver nitrate solution**: White, curdy ppt. of AgCl insoluble in water & in dil. nitric acid, but soluble in dilute ammonia solution.

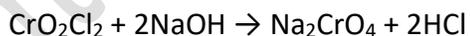
v) **Chromyl chloride test**: When a salt containing chloride ion is heated with K₂Cr₂O₇ and conc. H₂SO₄ orange red fumes of chromyl chloride (CrO₂Cl₂) are formed.



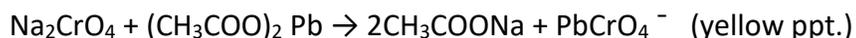
orange – red fumes

Chlorides of mercury, owing to their slight ionization, do not respond to this test and only partial conversion to CrO₂Cl₂ occurs with the chlorides of lead, silver, antimony and tin.

When chromyl chloride vapours are passed into sodium hydroxide a yellow solution of sodium chromate is formed which when treated with lead acetate gives yellow ppt. of lead chromate.



Yellow solution



8. Bromide (Br⁻)

i) **Conc. H₂SO₄** : Gives reddish brown vapours of bromine accompanying the hydrogen bromide.

ii) **Manganese dioxide and conc. sulphuric acid** : When a mix of solid bromide, MnO_2 and conc. H_2SO_4 is heated reddish brown vapours of bromine are evolved.



The following tests are performed with the aqueous salt solution.

iii) **Silver nitrate solution**: Pale yellow ppt. of silver bromide is obtained. This ppt. is sparingly soluble in dil but readily soluble in conc. ammonia solution and insoluble in dil. HNO_3 .

iv) **Lead acetate solution**: White crystalline ppt. of lead bromide which is soluble in boiling water.

9. Iodide (I^-)

i) **Conc. H_2SO_4** : Gives violet vapours of iodine

ii) **Silver nitrate solution**: Yellow ppt. of silver iodide AgI , very slightly soluble in conc. ammonia solution and insoluble in dil nitric acid.

10. Nitrate (NO_3^-)

i) **Conc H_2SO_4** : Gives reddish - brown vapours of nitrogen dioxide



ii) **Brown ring test**: When freshly saturated solution of iron (II) sulphate is added to nitrate solution and conc. H_2SO_4 is poured slowly down the side of the test - tube, a brown ring is obtained.



On shaking and warming the mix, the brown colour disappears, nitric oxide is evolved and a yellow solution of Iron(III) ions remains.

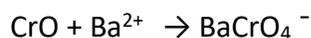
11. Sulphate (SO_4^{2-})

i) **Barium chloride solution**: White ppt. of barium sulphate BaSO_4 insoluble in warm dil. hydrochloric acid and in dilute nitric acid, but moderately soluble in boiling, conc. hydrochloric acid.

ii) **Mercury (II) nitrate solution**: Gives yellow ppt. of basic mercury (II) sulphate

12. Chromate CrO_4^{2-} and Dichromate (Cr_2O)

i) **Barium chloride solution:** Pale - yellow ppt. of barium chromate soluble in dilute mineral acids but insoluble in water and acetic acid.



Dichromate ion also gives the same ppt. but due to the formation of strong acid precipitation is partial.



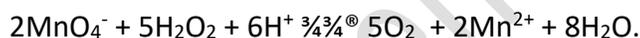
If sodium hydroxide or sodium acetate is added, precipitation becomes quantitative.

ii) **Silver Nitrate Solution:** Brownish - red ppt. of silver chromate Ag_2CrO_4 which is soluble in dil. nitric acid & in ammonia solution, but insoluble in acetic acid.

A reddish brown ppt. of silver dichromate $\text{Ag}_2\text{Cr}_2\text{O}_7$ is formed with a conc. solution of a dichromate.

13. Permanganate MnO

i) Hydrogen peroxide : It decolourises acidified potassium permanganate solution



ii) Iron (II) sulphate, in the presence of sulphuric acid, reduces permanganate to manganese (II). The solution becomes yellow because of the formation of iron (III) ions



Test For Cations:

Group	Group reagent	Ions	Colour & ppt.
Group I	dil HCl	$\text{Pb}^{2+}, \text{Hg}^+, \text{Ag}^+$	$\text{PbCl}_2, \text{Hg}_2\text{Cl}_2, \text{AgCl}$ - white
Group II	H ₂ S in dil HCl	$\text{Hg}^{2+}, \text{Cu}^{2+}, \text{Bi}^{3+}, \text{Cd}^{2+}$	Yellow- $\text{CdS}, \text{As}_2\text{S}_3,$
Group II A			$\text{As}_2\text{S}_5, \text{SnS}_2$
Group II B			Black - $\text{HgS}, \text{CuS}, \text{PbS}$
Group II B		$\text{As}^{3+}, \text{As}^{5+}, \text{Sb}^{3+}, \text{Sb}^{5+}, \text{Sn}^{2+}, \text{Sn}^{4+}$	Orange - $\text{Sb}_2\text{S}_3, \text{Sb}_2\text{S}_5$
			Brown - $\text{Bi}_2\text{S}_3, \text{SnS}$

Group III A	NH ₄ OH in presence of NH ₄ Cl	Fe ³⁺ , Al ³⁺ , Cr ³⁺	Fe(OH) ₃ , Al(OH) ₃ , Cr(OH) ₃ Brown White Green
Group III B	H ₂ S in presence of NH ₃ & NH ₄ Cl or (NH ₄) ₂ S.	Ni ²⁺ , Co ²⁺ , Mn ²⁺ , Zn ²⁺	ZnS - white or grey, Black - CoS, NiS MnS - Buff (light pink)
Group IV	(NH ₄) ₂ CO ₃ in presence of NH ₄ Cl & NH ₄ OH.	Ba ²⁺ , Sr ²⁺ , Ca ²⁺	BaCO ₃ , SrCO ₃ , CaCO ₃ - white
Group V	No common group reagent.	Mg ²⁺ , Na ⁺ , K ⁺ , NH ₄ ⁺	$\frac{3}{4}$

Group I (Pb²⁺, Ag⁺, Hg⁺)

(A) PbCl₂ gives a yellow ppt. with K₂CrO₄. The ppt. is insoluble in acetic acid but soluble in NaO

(B) PbCl₂ + 2KI → PbI₂ + 2KCl

(Yellow)

PbCl₂ + 2KI (excess) → K₂[PbI₄]

AgCl is soluble in NH₄OH forming a complex while Hg₂Cl₂ forms a black ppt. with NH₄OH.

AgCl + 2NH₄OH → Ag(NH₃)₂Cl + 2H₂O

Hg₂Cl₂ + 2NH₄OH → H₂NHgCl + Hg + NH₄Cl + 2H₂O

Amino mercuric Chloride

2. Group II A (Hg²⁺, Cu²⁺, Bi³⁺, Cd²⁺)

i) Hg²⁺ ions in solution, on addition of SnCl₂, give a white precipitate turning black.

2Hg²⁺ + SnCl₂ → Sn⁴⁺ + Hg₂Cl₂

White

Hg₂Cl₂ + SnCl₂ → SnCl₄ + 2Hg

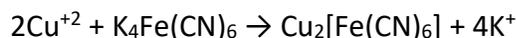
Black

ii) Cu^{+2} ions in solution give deep blue colour with excess of NH_4OH

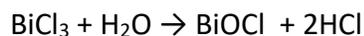


Deep blue in colour

Cu^{+2} ions give chocolate precipitate with $\text{K}_4\text{Fe}(\text{CN})_6$.

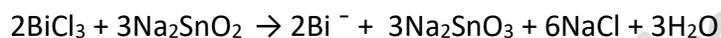


iii) Bi^{+3} ions in solution of HCl on addition of water give white cloudy precipitate.



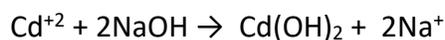
White ppt.

When treated with sodium stannite a black ppt. is obtained.



black

iv) Cd^{+2} ions in solution, with NaOH give a white precipitate.



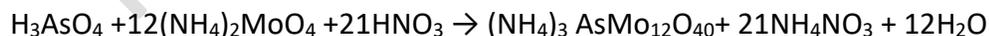
white

With ammonium hydroxide, Cd^{+2} ions give a white precipitate which dissolves in excess.



3. Group II B (As^{3+} , As^{5+} , Sb^{3+} , Sb^{5+} , Sn^{3+} , Sn^{4+})

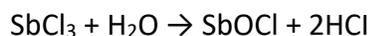
v) As^{+3} ions in solution give yellow precipitate with ammonium molybdate and HNO_3 on heating.



Yellow ppt.

vi) Sn^{+2} ions in solution as SnCl_2 give white ppt. with HgCl_2 , which turns black on standing.

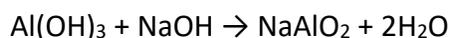
vii) Sb^{+3} ions in solution as SbCl_3 , on addition of water give white precipitate.



White

4. Group III A (Al^{3+} , Fe^{3+} , Cr^{3+})

1. White precipitate of $\text{Al}(\text{OH})_3$ is soluble in NaOH

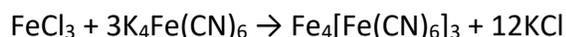


2. Precipitate of $\text{Cr}(\text{OH})_3$ is soluble in $\text{NaOH} + \text{Br}_2$ water and addition of BaCl_2 to this solution gives yellow precipitate.

$\text{Fe}(\text{OH})_3$ is insoluble in NaOH

3. Brown precipitate of $\text{Fe}(\text{OH})_3$ is dissolved in HCl and addition of KCNS to this solution gives blood red colour.

Also on addition of $\text{K}_4\text{Fe}(\text{CN})_6$ to this solution, a prussian blue colour is obtained.



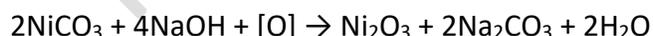
prussian blue colour

5. Group III B (Ni^{2+} , Co^{2+} , Mn^{2+} , Zn^{+2})

1. Ni^{+2} and Co^{+2} ions in solution, on addition of KHCO_3 and Br_2 water give apple green colour if Co^{+2} is present and black precipitate if Ni^{+2} is present.



Apple green colour



Black ppt.

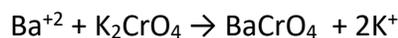
2. Zn^{+2} ions in solution give white precipitate with NaOH , which dissolve in excess of NaOH .

3. Mn^{+2} ions in solution give pink precipitate with NaOH turning black or brown on heating.

6. Group IV (Ba^{2+} , Sr^{2+} , Ca^{2+})

Ba^{2+} ions in solution give

(A) Yellow precipitate with K_2CrO_4



Yellow

(B) White precipitate with $(\text{NH}_4)_2\text{SO}_4$

Sr^{2+} ions give white precipitate with $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$

Ca^{2+} ions give white precipitate with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ only.

7. Group V (NH_4^+ , Na^+ , K^+ , Mg^{2+})

All ammonium salts on heating with alkali say NaOH give a colourless gas with a pungent smell (NH_3)

(A) Gas evolved gives white fumes with HCl

(B) Paper soaked in CuSO_4 solution, is turned deep blue by NH_3 due to complex formation

(C) With $\text{Hg}_2(\text{NO}_3)_2$, a black colour is obtained



black

(D) With Nessler's reagent (alkaline solution of potassium tetraiodomercurate(II)), a brown ppt. is obtained

Potassium salts give yellow ppt. with sodium cobalt nitrite

Sodium salts give a heavy white ppt. with potassium dihydrogen antimonate

Mg^{2+} gives white ppt. of magnesium hydroxide with sodium hydroxide