Qualitative Inorganic Analysis

The investigation and recognition of substances is a very important branch of chemistry, and the skill of the analyst is essential today in medicine, criminology and the manufacture of countless products.

Qualitative inorganic analysis is concerned with the identification of radicals present in an inorganic salt or a mixture of salts. Simple tests are available for showing the presence of these radicals. The tests are carried out in right order.

Inorganic salts are formed when acids react with bases. Each inorganic salt consists of two parts, i.e. part contributed by acid is called acidic radical or anion and the part contributed by base is called basic radical or cation. For example, in sodium chloride. Na^+ is basic radical or cation and Cl^+ is acidic radical or anion

Before you start the test of an inorganic substance always note the appearance of the substance (colour, state). and determine if it is soluble in water. If it is, test with litmus to see if the solution is acidic, alkaline or neutral. Colour and solubility of inorganic substance in water may help to identify some basic and acidic radicals.

Table 7.1 Colour of some inorganic salts

Colour	Compounds
White or colourless	Salts of Na, K, NH, Mg, Ca, Sr, Ba, Zn, and Al
Blue	Hydrated cupric salt and anhydrous cobalt salt
Pink	Hydrated salt of Co and Mn
Green	Fe (ous) salt, except FeS, $CuCl_2$, $2H_2O$, $CuCO_3$ N (ous) salt
Black	FeS, CoS, NiS, PbS

Table 7.2 Solubility of inorganic compounds in water

Compounds	Solubility in Water
Nitrates	All salts are soluble
Sulphates	All except Pb, Fe(ic), Ba, Sr and Ca
Nitrites	All except Ag
Chlorides Bromides and iodides	All Chlorides Bromides and iodides except and
Carbonates	Na, K and NH: only
Sulphate	Na, K and NH: only
	Na, K and NH: only

The qualitative analysis of an inorganic substance is generally carried out in the following four parts

1. Dry test for Basic Radicals
2. Dry test for Acidic Radicals
3. Wet test for anions(acidic radicals)
4. Wet test for anions(acidic radicals)

·Aim: To determine acid and basic radical in a given salt sample.
Physical characteristic:
(1) colour –
(2) odour –
(3) solubility –
(4) physical appearance –

(A) Dry tests for basic radicals

Action of heat

Perform thus experiment by heating a small amount of salt in a dry test tube.

Information from this test can give valuable clues, partly from observation of the residue partly from identification of any gas evolved. Tabulate your observation along with the inferences that you can draw

Experiment	Observation	Inference
heat a pinch of the solid in a dry test tube	1) (Residue) Change in colour i. Yellow when hot, white when cold ii. Yellow in both hot and cold conditions iii. Red while hot and yellow or brown when cold. iv. Black in both and cold conditions	Zn^{2+} Pb^{2+} Fe^{3+} salt of Cu^{2+}, Co^{2+}, Mn
	2) Salt fuses *melting*	Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}
	3) Decrepitation The salt decrepitates (flies to pieces with sharp crackling sound)	$Pb(NO_3)_2$. NaCl
	4) Formation of sublimate *(Fog like Formation)* White sublimate formed	NH_4^+
	5) Evolution of gases i. Colourless and odourless gas, turns lime water milky	CO^{2-}_3 or $C_2O_4^{3-}$ present
	ii. Evolution of ammonia-gives white fumes when a glass rod dipped in dil HCl is brought near the mouth of the test tube	NH_4^+

(B) Dry tests for acid radicals

Dry rests for acid radicals are performed in the following manner

1) Action of diluted hydrochloric and
2) Action of concentrated sulphuric acid

1. Action of dil. hydrochloric acid

Experiment	Observation	Inference
Take a small amount of the substance and add 5 ml of dil hydrochloric acid, If no reaction takes place, warm a little	i. Colourless and odourless gas is evolved with effervescence, turns lime water milky. ii. Colourless gas with odour of rotten eggs turns lead acetate paper black. iii. Colourless gas possessing suffocating odour, turns acidified potassium dichromate solution green iv. Reddish-brown gas is evolved turns acidified Starch-iodide paper blue (starch-iodide paper is prepared by moistening a piece of filter paper with a KI solution and then with a starch solution). v. Colourless gas with smell of vinegar	Carbonate(CO_3^{2-}) and Bicarbonate(HCO_3^-) Sulphate(S^{2-}) Sulphite(SO_3^{2-}) Nitrite(NO_2^-) Acetate(CH_3COO^-)

2.Action of concentrated sulphuric acid

Experiment	Observation	Inference
1) Take a small amount of the substance in a dry test tube. Add 4-5 ml, of concentrated H_2SO_4, and gently heat the solution.	i. Colourless gas with pungent smell gives white fumes when glass rod moistened with NH_4OH is held near the mouth of the test tube. ii. Reddish brown gas is evolved. iii. Violet vapours are evolved turns starch paper blue iv. Browns fumes evolved.	Chloride (CL^-) Bromide(Br^-) Iodide(I^-) Nitrate(NO_3^-)

2) Take small amount of substance in a dry test tube. Add a little MnO_2 and 2 ml. conc. H_2SO_4. Heat gently	i. Greenish-yellow gas turns moist starch-iodide paper blue. ii. Brown-red vapours turn starch-iodide paper blue. iii. Violet vapours turns starch paper blue.	Chloride (CL^-) Bromide(Br^-) Iodide(I^-)
3) Take a small amount of the substance in a dry test tube. Add 3-4 ml conc. H_2SO_4, and a little Cu turning. Heat gently	Reddish-brown fumes and the solution in the test tube appear blue.	Nitrate(NO_3^-)

(c) Wet test for acid radical

If salt not soluble in H_2O then prepare Na_2Co_3 extract. Otherwise water extract

Experiment	Observation	Inference
1. Take about 5 ml of Na_2CO_3 extract in a test tube. Acidify with dil.HCl .Boil to expel CO. Add $BaCl_2$ solution.	White ppt insoluble in dil HCl or dil HNO_3	Sulphate (SO_4^{2-})
	White ppt.	Sulphite(SO_3^{2-})
2. Take 5 ml of sodium carbonate extract in a test tube. Acidify with dil. HCl. Add $BaCl_2$ solution followed by bromine water. Heat the content		
	A brown ring at the junction of the two liquids.	Nitrate(NO_3^-)
3. Take 5 ml of sodium carbonate extract in a test tube. Acidify with dil H_2SO_4. Add about 5 ml of freshly prepared $FeSO_4$ solution. Slowly pour 2-3 ml of conc. H_2SO_4 down the side of the tube. Hold the		

tube at an angle while doing this. The heavy Sulphuric acid sinks to the bottom.		
4. Take 5ml of Na_2CO_3 extract in a test tube. Acidify with dil HNO_3 Boil off CO_2 Add $AgNO_3$ solution.	White ppt. readily soluble in NH_4OH.	Chloride(Cl^-)
	Or	
	Pale yellow ppt. soluble in conc NH_4OH solution.	Bromide(Br^-)
	Or	
	Yellow ppt. insoluble in conc NH_4OH	Iodide (I^-)
5. Take 5 ml of Na_2CO_3 extract. Acidify with acetic acid and then add lead acetate solution.	Black ppt soluble in hot dil HNO_3.	Sulphide (S^{2-})
6. Take 5 ml of Na_2CO_3 extract; add a few drops of sodium nitro prusside solution.	Violet or Pink colouration	Sulphide (S^{2-})
7. Take 2-3 ml Na_2CO_3 extract in a test tube. Acidify with dil H_2SO_4 Then add KI solution.	Reddish-brown colouration, turns starch solution blue.	Nitrate (NO_2^-)
8. Take 5 ml of Na_2CO_3 extract in a test tube Add 2-3 ml of conc. HNO_3 and 10 ml of ammonium molybdate solution Warm moderately (40°C)	Straw-coloured ppt (light yellow)	Phosphate (PO_4^{3-})
9. Take 2-3 ml of Na_2CO_3 extract in a test tube Acidify with dil acetic acid Add $CaCl_2$ solution.	White ppt soluble in dilute HCl	Oxalate ($C_2O_4^{2-}$)
10. Dissolve salt in water: To the aqueous solution add freshly	Blood red colouration	Acetate (CH_3COO^-)

prepared $FeCl_2$ solution.		

(D) Wet test for basic radical

1. Distilled water (cold/hot)
2. Dil HCl (cold/hot)
3. Conc HCl (cold hot)

Solubility of inorganic salt in above solvents may often help to identify some basic radicals

Solvent	Salt
1. Cold water	a) All NH_4, Na and K salts b) All nitrites, nitrates and acetates c) Most of the sulphates except those of Pb, Ba, Ca, Sr. d) All chlorides except that of lead
2. Hot water	Lead chloride, lead nitrate All carbonates which do not dissolve in water, i.e. carbonates of Ca, Ba, Sr, Mg, Fe, etc but not of Pb

The usual procedures for analyzing a salt involve systematic separation of basic radical into group. The table given below gives briefly the classification of basic radicals into groups reagents and the form in which they are precipitated.

Group	Group Reagent	Basic Reagent	Form in which basic radicals are precipitated
I	Dil HCl	Pb^{2+}, Hg^{2+}(ous), Ag^{+}	Chlorides
II	H_2S in presence of dil HCl	Pb^{2+}, Cu^{2+}, As^{3+}, Hg^{2+},Cd^{2+}, Bi^{3+}, Sb^{3+}, Sn^{2+}	Sulphides
III	NH_4OH in presence of NH_4Cl	Fe^{3+}, Al^{3+}, Cr^{3+}	Hydroxides
IV	H_2S in presence of NH_4OH	Ni^{2+},Mn^{2+},Zn^{2+},Co^{2+}	Sulphides
V	$(NH_4)_2C0_3$ in the presence of NH_4OH	Ca^{2+}, Sr^{2+} , Be^{2+}	Carbonates
VI	—	Mg^{2+}, Na,K	—

(Metal ions in the box are not included in the syllabus)

Division of the basic radicals (cations) in different groups (group seperstion)

Experiments	Observation	Inference

1. Add dilHCl to the salt solution.	White ppt.	Group I present.
2. Add dil HCl to the salt solution and then pass H^2S gas.	Black ppt.	Group II present.
3. Boil salt solution with salt + HCl and add NH_4Cl and NH_4OH solution in excess.	(a)Reddish-brown ppt. (b)White gelatinous ppt.	Group III present (a)Fe salt (b)Al salt
4. Add NH_4Cl and NH_4OH to salt solutionand pass H_2S gas.	(a)Black ppt. (b)Pink ppt. (c)White ppt.	Group IV present (a)Co salt (b)Mn salt (c)Zn salt
5. Add NH_4OH and $(NH_4)_2CO_3$ to the salt solution.	White ppt.	Group V present maybe Ca, Ba, Sr salt.
6. No particular group reagent.		Group VI Mg salt.
7. ~~Salt solution + Conc. NaOH~~	~~(a) An pungent smell (b)White fumes becomes dense when glass rod dipped in dil. HCL is brought near the Mouth.~~	

Group analysis:

Analysis of Group Zero :-

Experiment	OBSERVATION	INFERENCE
1. Heat salt + NaOH + Boing a glass rod dipped in dil HCl near the mouth of test tube	dense white fumes	NH_4^+ present
2. Heat salt + NaOH + Nessler reagent	Brown ppt	NH_4^+ confirmed.

Reaction :

$$NH_4^+ + 2[HgI_4]^{2-} + 4OH^- \longrightarrow \underset{\text{(brown ppt)}}{HgO \cdot Hg(NH_2)I \downarrow} + 7I^- + 3H_2O$$

Analysis of Group 1.

Exp	OBSE	INF
sample + few drops of K_2CrO_4	yellow ppt	Pb^{2+} confirmed.

Reaction:

$$Pb^{2+} + CrO_4^{2-} \rightarrow PbCrO_4$$
(yellow ppt)

This yellow ppt is soluble in hot NaOH solution.

$$PbCrO_4 + 4NaOH \rightleftharpoons Na[Pb(OH)_4] + Na_2CrO_4$$

Analysis of Group II

Dissolve and filter black ppt.

Exp	OBS	INF
Boil the black ppt + dil HNO_3 + dil H_2SO_4. If no white ppt then add excess of NH_4OH solution to the solution (1)	white ppt is formed	Pb^{2+} present
	deep blue colour is observed.	Cu^{2+} present

Reaction:

$$Cu^{2+} + SO_4^{2-} + 2NH_3 + 2H_2O \rightarrow \underset{\text{blue ppt}}{Cu(OH)_2 \cdot CuSO_4} + 2NH_4^+$$

Analysis of Group III (brown ppt) (gelatinous ppt)

EXPERIMENT	OBSERVATION	INFERENCE
(1) Filter the brown ppt and dissolve the ppt in dil HCl and add Potassium ferrocyanide test	blue colour	Fe^{3+} present
(2) Dissolve white ppt in dil HCl + NH_4OH	Blue ppt	Al^{3+} present

Reaction: $4FeCl_3 + 3K_4[Fe(CN)_6] \rightarrow 12KCl + Fe_4[Fe(CN)_6]_3$

blue colour

$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$

$AlCl_3 + 3NH_4OH \rightarrow 3NH_4Cl + Al(OH)_3$ (Blue colour)

Analysis of Group IV

(a) Filter the ppt (black ppt) and add NH_4OH and add acetic acid and potassium nitrite — yellow ppt — Co^{2+} present.

(b) black ppt + NH_4OH + dimethyl/ethyl glyoxime → Rose Red ppt → Ni^{2+} present

(c) black ppt + NaOH (excess) + Br_2 water + boil → black ppt → Ni^{2+} present.

flesh coloured ppt + add NaOH + shake + white ppt is formed + add Br_2 water to white ppt → ppt turns black or brown → Mn^{2+} present.

Dull white ppt + NaOH + white ppt is formed + NaOH + white ppt dissolves → Zn^{2+} present.

Dull white ppt + pot. ferrocyanide soln + white or bluish white ppt is formed → Zn^{2+} present.

Co^{2+} : $CoCl_2 + 2KNO_2 \rightarrow 2KCl + Co(NO_3)_2$

$KNO_2 + CH_3COOH \rightarrow CH_3COOK + HNO_2$

$Co(NO_2)_2 + 2HNO_2 \rightarrow Co(NO_2)_3 + H_2O + NO$

$Co(NO_2)_3 + 3KNO_2 \rightarrow K_3[Co(NO_2)_6]$

Ni^{2+} : $NiCl_2 + 2NaOH \rightarrow 2NaCl + Ni(OH)_2$

$Br_2 + H_2O \rightarrow 2HBr + [O]$

$2Ni(OH)_2 + H_2O + [O] \rightarrow 2Ni(OH)_3$

Mn^{2+} : $MnCl_2 + 2NaOH \rightarrow Mn(OH)_2 + 2NaCl$.

Zn^{2+} : $2ZnCl_2 + K_4[Fe(CN)_6] \rightarrow Zn_2[Fe(CN)_6] + 4KCl$

Analysis of Group V)

White ppt + dissolves the ppt in hot dil CH_3COOH + divide the solution into three parts.

First part + potassium Chromate → yellow ppt → Ba^{2+} confirmed.

Second part + $(NH_4)_2SO_4$ → white ppt → Sr^{2+} present

Third part + Ammonium oxalate + Ammonium hydroxide → white ppt → Ca^{2+} present.

Ba^{2+} : $BaCO_3 + 2CH_3COOH \rightarrow (CH_3COO)_2Ba + CO_2 \uparrow + H_2O$

$(CH_3COO)_2Ba + K_2CrO_4 \rightarrow 2CH_3COOK + BaCrO_4$

Sr^{2+} : $SrCO_3 + 2CH_3COOH \rightarrow (CH_3COO)_2Sr + CO_2 + H_2O$

$(CH_3COO)_2Sr + (NH_4)_2SO_4 \rightarrow 2CH_3COONH_4 + SrSO_4$

Ca^{2+} : $CaCO_3 + 2CH_3COOH \rightarrow (CH_3COO)_2Ca + CO_2 + H_2O$

$(CH_3COO)_2Ca + (NH_4)_2C_2O_4 \rightarrow 2CH_3COONH_4 + CaC_2O_4$

Analysis of group VI

Sample + NH_4Cl + NH_4OH + ammonium phosphate sol^n + rub the sides of the test tube with a glass rod → white ppt → Mg^{2+} present.

Reaction :

$MgCl_2 + NH_4OH + (NH_4)_2HPO_4 \rightarrow Mg(NH_4)PO_4 + 2NH_4Cl + H_2O$.