Qualitative Analysis

Analytical chemistry deals with qualitative and quantitative analysis of the substances. In inorganic qualitative analysis, the given compound is analyzed for the radicals, i.e., cation and the anion, that it contains. Physical procedures like noting the colour, smell or taste of the substance have very limited scope because of the corrosive, poisonous nature of the chemical compounds. Therefore, what one has to resort to is the chemical analysis of the substance that has to be carried out along with the physical examination of the compound under consideration.

The common procedure for testing any unknown sample is to make its solution and then test this solution for the ions present in it. There are separate procedures for detecting cations and anions, therefore qualitative analysis is studied under cation analysis and anion analysis. The systematic procedure for qualitative analysis of an inorganic salt involves the following steps :

(a) Preliminary tests

1. Physical appearance (colour and smell).
2. Dry heating test.
3. Charcoal cavity test.
4. Charcoal cavity and cobalt nitrate test.
5. Flame test.
6. Borax bead test.
7. Dilute acid test.
8. Potassium permanganate test.
9. Concentrated sulphuric acid test.
10. Tests for sulphate, phosphate and borate.

(b) Wet tests for acid radical.

(c) Wet tests (group analysis) for basic radical.

Physical Examination Of The Salt

The physical examination of the unknown salt involves the study of colour, smell and density. The test is not much reliable, but is certainly helpful in identifying some coloured cations. Characteristic smell helps to identify some ions such as ammonium, acetate and sulphide. (See Table 9.1 on next page)

Note :

1. If you have touched any salt, wash your hands at onte. It may be corrosive to skin.
2. Never taste any salt, it may be poisonous. Salts of arsenic and mercury are highly poisonous.
3. Salts like sodium sulphide, sodium nitrite, potassium nitrite, develop a yellow colour.

Table 9.1. Physical Examination

Experiment	Observations	Inference
1. Colour	Blue or Bluish green	Cu^{2+}
	Light green	Fe^{2+}
	Dark brown	Fe^{3+}
	Green	Ni^{2+}
	Pink	Co^{2+}
	Light pink, flesh colour or earthy colour	Mn^{2+}
	White	Shows the absence of Cu^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, CO^{2+}
2. Smell	Ammoniacal smell	NH_4^+

Take a pinch of the salt between your fingers and rub with a drop of water	Vinegar like smell Smell like that of rotten eggs	$CH3COO^-$ S^{2-}
3. Density	(i) Heavy (ii) Light fluffy powder	Salt of Pb^{2+}, or Ba^{2+} Carbonate
4. Deliquescence	Salt absorbs moisture and becomes paste like	(i) If coloured, may be $Cu(NO_3)_2$, $FeCl_3$. (ii) If colourless, may be $Zn(NO_3)_2$, chlorides of Zn^{2+}, Mg^{2+} etc.

Dry Heating Test

This test is performed by heating a small amount of salt in a dry test tube. Quite valuable information can be gathered by carefully performing and noting the observations here. On heating some salts undergo decomposition thus evolving the gases or may undergo characteris¬tic changes in the colour of residue. These observations are tabulated below (Table 9.2) along with the inferences that you can draw.

Table 9.2. Dry Heating Test

Observations	Inference
1. Gas evolved	
(a) **Colourless and odourless gas**	CO_3^{2-} or C_2O_4

CO_2 gas turns lime water milky	
(b**) Colourless gas with odour**	
(i) H_2S gas—Smells like rotten eggs, turns lead acetate paper black.	Hydrated S^{2-}
(ii) SO_2 gas—Smells like burning sulphur, turns acidified potassium dichromate paper green	SO_3^{2-}
(iii) HCl gas—Pungent smell, white fumes with ammonia, white ppt with silver nitrate solution.	Cl^-
(iv) Acetic acid vapours—Characteristic vinegar like smell.	CH_3COO^-
(v) NH_3 gas—Characteristic smell, turns Nessler's solution brown.	NH_4^+
(c) **Coloured gases**—Pungent smell	
(i) NO_2 gas—Reddish brown, turns ferrous sulphate solution black.	NO^{2-} or NO^{3-}
(ii) Cl_2 gas—Greenish yellow, turns starch iodide paper blue.	Cl^-
(iii) Br_2 vapours—Reddish brown, turns starch	Br^-

paper orange yellow. (iv) I_2 vapours—Dark violet, turns starch paper blue.	I^-
2. Sublimate formed (a) White sublimate (b) Black sublimate accompanied by violet vapours	 NH_4^+ I^-
3. Decrepitation The salt decrepitates.	A salt having no water of crystallisation. For example, $Pb(NO_3)_2$, NaCl, KBr.
4. Swelling The salt swells up into voluminous mass.	 PO_4^{3-} indicated
5. Residue (i) Yellow when hot white when cold (ii) Brown when hot and yellow when cold (iii) White salt becomes black on heating (iv) White residue, glows on heating (v) Original salt blue becomes white on heating	Zn^{2+} Pb^{2+} CH_3COO^- indicated Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, etc. Hydrated $CuSO_4$ indicated CO^{2+}, Cu^{2+}, Mn^{2+} indicated.

(vi) Coloured salt becomes brown or black on heating.	

Note:

1. Use a perfectly dry test-tube for performing this test. While drying a test-tube, keep it in slanting
position with its mouth slightly downwards so that the drops of water which condense on the upper cooler parts, do not fall back on the hot bottom, as this may break the tube. ,
2. For testing a gas, a filter paper strip dipped in the appropriate reagent is brought near the mouth of the test tube or alternatively the reagent is taken in a gas-detector and the gas is passed through it [Fig. 9.1].

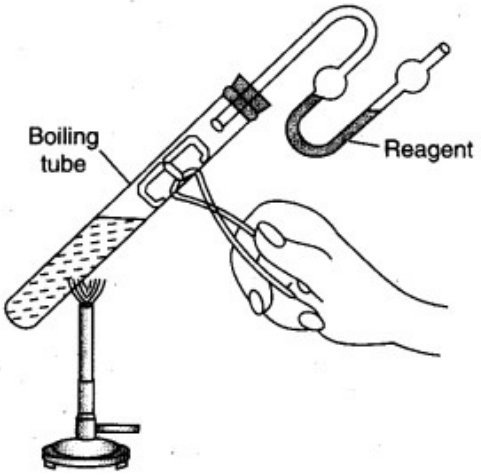


Fig. 9.1. Testing a gas

3. Do not heat the tube strongly at one point as it may break.

Charcoal Cavity Test

This test is based on the fact that metallic carbonates when heated in a charcoal cavity decom¬pose to give corresponding oxides. The oxides appear as coloured incrustation or residue in the cavity. In certain cases, the oxides formed partially undergo reduction to the metallic state producing metallic beads or scales.

Examples :

(a)

$$ZnSO_4 + Na_2CO_3 \longrightarrow ZnCO_3 + Na_2SO_4$$

$$ZnCO_3 \longrightarrow ZnO + CO_2 \uparrow$$

Yellow when hot, white when cold

(b)

$$Pb(NO_3)_2 + Na_2CO_3 \longrightarrow PbCO_3 + 2NaNO_3$$

$$PbCO_3 \longrightarrow PbO + CO_2 \uparrow$$

$$PbO + C \longrightarrow Pb + CO \uparrow$$

Bead

(c)

$$CuSO_4 + Na_2CO_3 \longrightarrow CuCO_3 + Na_2SO_4$$

$$CuCO_3 \longrightarrow CuO + CO_2 \uparrow$$

$$CuO + C \longrightarrow Cu + CO \uparrow$$

Reddish scales

Procedure

While performing charcoal cavity test, make a small cavity on a charcoal block with the help of borer as shown in Fig. 9.2. Mix small amount of salt with double its quantity of sodium carbonate. Place it in the cavity made on the block of charcoal. Moisten with a drop of water and direct the reducing flame of the bunsen burner on the cavity by means of a mouth blowpipe as shown in Fig. 9.3. Heat strongly for sometime and draw inference according to the Table 9.3.

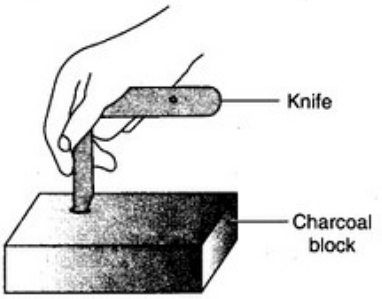


Fig. 9.2. Making bore on a charcoal block.

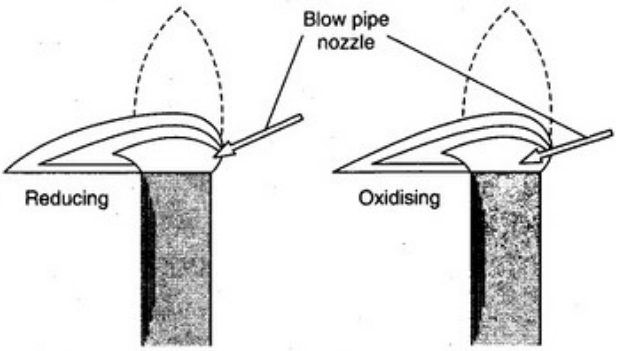


Fig. 9.3. Directing flame with blow pipe.

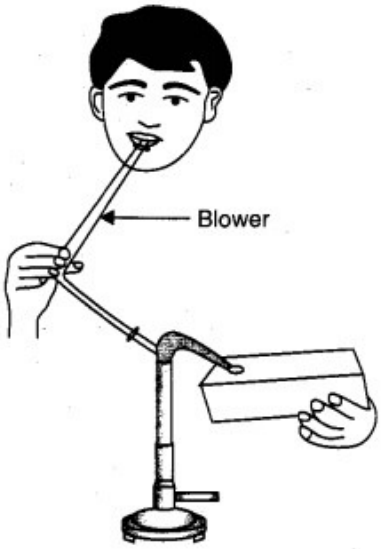


Fig. 9.4. Blowing flame on the cavity.

Table 9.3 Charcoal Cavity Test

Observations			**Inference**
Incrustation or Residue		**Metallic bead**	
Hot	**Cold**		
Yellow	White	None	Zn^{2+}
Brown	Yellow	Grey bead which marks the paper	Pb^{2+}
None	None	Red beads or scales	Cu^{2+}
White residue which glows	None	None	Ba^{2+}, Ca^{2+}, Mg^{2+}
Black	None	None	Nothing definite—generally coloured salt

To obtain a reducing flame with the help of a mouth blow pipe, make the bunsen burner flame luminous by closing the air holes of the burner. Keep the nozzle of the blow pipe just outside the flame (Fig. 10.4) and blow gently on to the cavity.

Cobalt Nitrate Test

This test is applied to those salts which leave white residue in charcoal cavity test.
The test is based on the fact that cobalt nitrate decomposes on heating to give cobalt oxide, CoO. This combines with the metallic-oxides, present as white residue in the charcoal cavity forming coloured compounds. For example, when a magnesium salt undergoes charcoal cavity test, a white residue of MgO is left behind. This on treatment with cobalt nitrate and subsequent heating forms a double salt of the formula MgO.CoO which is pink in colour. In addition to metallic oxides, phosphates and borates also react with cobalt oxide to form $Co_3(PO_4)_2$ and $Co_3(BO_3)_2$ which are blue in colour.
Some of the reactions involved are given below :

$$2Co(NO_3)_2 \xrightarrow{\Delta} 2\,CoO + 4NO_2 + O_2$$

(i) Zinc salt :

$$ZnO + CoO \longrightarrow ZnO.CoO\ (Green)$$

(ii) Magnesium salt :

$$MgO + CoO \longrightarrow MgO.CoO\ (Pink)$$

Procedure

Put one or two drops of cobalt nitrate solution on the white residue left after charcoal cavity test. Heat for one or two minutes by means of a blow pipe in oxidising flame. Observe the colour of the residue and draw inferences from Table 9.4.

Table 9.4. Cobalt Nitrate-Charcoal Cavity Test

Color of the Residue	Inference
Green	Zn^{2+}
Pink	Mg^{2+}
Blue	PO_4^{3-}
Black	It is due to the formation of CoO. No definite indication.

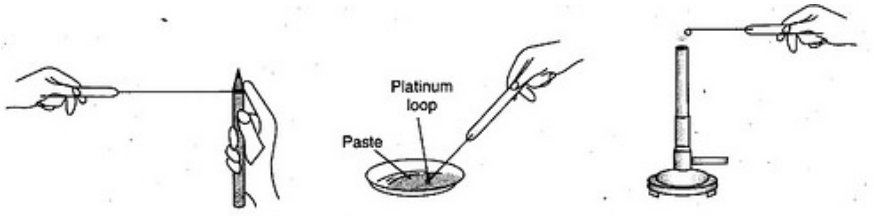
Note:

1. Perform this test only if the residue in the charcoal cavity test is white.
2. Do not put more than 2 drops of cobalt nitrate on the white residue. Excess cobalt nitrate may decompose to give cobalt oxide which is black in colour.
3. Use dilute solution of cobalt nitrate.

Flame Test

Certain salts on reacting with cone. HCl from their chlorides, that are volatile in non-luminous flame. Their vapours impart characteristic colour to the flame. This colour can give reliable information of the presence of certain basic radicals.

For proceeding to this test, the paste of the mixture with cone. HCl is introduced into the flame with the help of platinum wire (Fig. 9.5).



(a) Making a loop of platinum wire. (b) Dipping the platinum wire in the paste of salt and HCl. (c) Introducing the wire in the flame.

Fig. 9.5. Flame test.

Procedure

Clean the platinum wire by dipping it in some cone. HCl taken on a watch glass and then heating strongly in the flame. This process is repeated till the wire imparts no colour to the flame. Now prepare a paste of the salt with cone. HCl on a clean watch glass. Place small amount of this paste on platinum wire loop and introduce it into the flame. Note the colour imparted to the flame with naked eye and through blue glass.

Table 9.5. Flame Test

Color of the Flame		**Inference**
With naked eye	**Through blue glass**	
1. Brick-red (not persistent)	Light yellowish green	Ca^{2+}
2. Crimson-red (persistent)	Crimson	Sr^{2+}
3. Persistent grassy-green (appears after prolonged heating)	Green	Ba^{2+}
4. Bright-bluish green	Visible	Cu^{2+}
5. Green flashes		Zn^{2+} and Mn^{2+} salts
6. Dull bluish-white	White	Pb^{2+}

Note: Sodium salts impart golden yellow colour to the flame while potassium salts impart pink violet colour. However, in the present context Na^+ and K^+ salts are not in the syllabus.