4. Chromate CrO_4^{--}. This can be tested by following methods :

(*i*) To an aqueous solution, add barium chloride solution. A pale yellow precipitate insoluble in acetic acid indicates the presence of chromate.

(*ii*) To an aqueous solution or solution in acetic acid, add silver nitrate solution. A brownish red precipitate of silver chromate is obtained.

(*iii*) Treat its acidic solution with H_2O_2. This gives deep blue solution of chromium pentoxide which fades quickly on standing.

(*iv*) In acidic solution, pass H_2S gas. This turns the solution green.

(*v*) Acidify the solution with dilute H_2SO_4 or acetic acid and add diphenyl carbazide reagent. A deep blue colouration is produced.

5. Permanganate, MnO_4^-. All permanganates are, as a rule, soluble in water imparting purple solution. Following tests can be applied to ascertain the presence of permanganate radical.

(*i*) To an aqueous solution, add concentrated HCl and boil. Chlorine gas is evolved which turns starch–iodide paper blue.

(*ii*) To concentrated aqueous solution, add NaOH solution and warm the mixture, A green solution is obtained with the liberation of oxygen gas. The green solution when poured into a beaker full of water and contents acidified, purple colours of permanganate is restored.

6. Arsenate, AsO_4^{3-} (*i*) To a neutral solution of arsenate, add silver nitrate solution. A brownish red precipitate insoluble in acetic acid but soluble in mineral acid and in ammonia indicates the presence of arsenate.

(*ii*) To an aqueous solution, add nitric acid and ammonium molybdate. Boil the mixture. A yellow crystalline precipitate of ammonium arsenomolybdate, $(NH_4)_3AsMo_{12}O_{40}$ indicates the presence of arsenate. This precipitate is soluble in ammonia and in alkalies. The ionic equation for the above test is written as :

$$AsO_4^{3-} + 12MoO_4^{2-} + 3NH^{4+} + 24H^+ \longrightarrow \underset{\text{precipitate}}{(NH_4)_3AsMo_{12}O_{40}\downarrow} + 12H_2O$$

(*iii*) Acidify the solution with large amount of concentrated HCl and to it, add KI solution. This will precipitate iodine which can be tested as usual. The ionic equation is :

$$AsO_4^{3-} + 2H^+ + 2I^- \rightleftharpoons AsO_3^{3-} + I_2\downarrow + H_2O$$

2·6. Tests with sodium carbonate extract

A large number of acid radicals can be confirmed by using sodium carbonate extract of the mixture. This is especially useful when the mixture is less soluble in dilute acids. For example, many halides and sulphates do not readily dissolve in acids and hence they may not be tested.

When mixture is heated strongly in the minimum quantity of water with excess of Na_2CO_3, the double decomposition takes place *i.e.*, the partner radicals are changed. Sodium joins with anions of mixture and carbonate attaches with basic radicals of mixture. After heating, it is mixed with water where sodium salts which contain anions of mixture dissolve (as sodium salts are soluble) and carbonates of the metals remain as insolubles. In this way, we separate the anions from the cations of the mixture after filtration.

Preparation of Sodium Carbonate Extract

Take one part of mixture and four parts of pure Na_2CO_3 in a porcelain dish. Add 15-20 ml distilled water and heat while stirring with the glass rod. Heat it to boiling gently for about 5-10 minutes, add water to make up the loss by evoparation and filter. The filtrate is the desired sodium carbonate extract. Use 1-2 ml of this extract for each test.

Precautions

1. Certain substances may remain undecomposed by boiling with Na_2CO_3. They include certain phosphates, fluorides and silver halides. Hence if corresponding anions are not found in the prepared soda extract, they should be tested in the residue left by action of Na_2CO_3 or in certain instances, in separate portion of original mixture.

2. During neutralization of soda extract with acids, sometimes there appears ppt. though it becomes soluble in excess of acid. It is desirable to filter off such a ppt. This is because the cations forming amphoteric oxides may partially pass into soda extract (*e.g.* AlO_2^-). The copper ion forms a complex compound and also partially passes in soda extract colouring it bluish. On subsequent neutralization, all these compounds are decomposed and corresponding cations are precipitated, *e.g.*,

$$NaAlO_2 + CH_3COOH + H_2O \longrightarrow Al(OH)_3 \downarrow + CH_3COONa$$

Similarly, copper is precipitated as basic carbonate.

3. Before adding a particular reagent to test acid radicals, extract must be made acidic because carbonate should be decomposed otherwise confusion may arise due to precipitation of the carbonates of the metals. For example, in test for sulphate, we add $BaCl_2$ solution to acidified sodium carbonate extract. The appearance of white ppt. indicates the presence of SO_4^{2-} radical. If sufficient acid is not added prior to the addition of $BaCl_2$, some undecomposed sodium carbonate will remain in solution. This will give a white ppt. of $BaCO_3$ even in absence of SO_4^{2-}. This will obviously create a confusion.

Hence in testing various radicals by the sodium carbonate extract, acidify according to the following chart:

Radicals to be tested	*Acid used for neutralization*	*Reagent for precipitation*
Chloride	dil. HNO_3	$AgNO_3$
Bromide	"	"
Iodide	"	"
Sulphate	dil. HCl	$BaCl_2$
Oxalate	CH_3COOH	$CaCl_2$

(4) Do neutralization very carefully, shaking the liquid thoroughly after each addition and avoid an excess of acid otherwise certain anions (*e.g.*, S^{2-}, NO_2^- etc.) may also be lost.

2·7. Combination Tests of Acid Radicals

Generally the following combinations are given :

1. Sulphide, Sulphite, Sulphate and Thiosulphate
2. Nitrite and Nitrate
3. Nitrite and Iodide
4. Nitrite and Sulphide
5. Nitrate in presence of Bromide and Iodide
6. Chloride, bromide and Iodide
7. Oxalate and Fluoride
8. Carbonate and oxalate
9. Carbonate in presence of Sulphite
10. Sulphite and Fluoride
11. Phosphate, Arsenate and Arsenite

All the combinations are not essential to be tested ; the radicals which respond test in preliminary examination, their combinations are to be seen and carried out.

1, Sulphide, sulphite, sulphate and thiosulphate present

Systematic analysis is required for detection of S^{2-}, $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} ions when present together, because some of these interfere in test of others. For example, if the solution contains S^{2-}

and SO_3^{2-}, addition of acid liberates H_2S and SO_2 simultaneously and the two immediately interact.

$$SO_2 + 2H_2S \longrightarrow 3S\downarrow + 2H_2O$$

As a result of this reaction, only the gas present in excess will be detected. If this gas is SO_2, addition of acid would be accompanied by the same effects (formation of SO_2 and S) as would be observed if the solution contained $S_2O_3^{2-}$. Thiosulphate would, therefore, be wrongly found. It is obvious that a mixture of SO_3^{2-} and $S_2O_3^{2-}$ would behave on acidification in the same way as $S_2O_3^{2-}$ by itself.

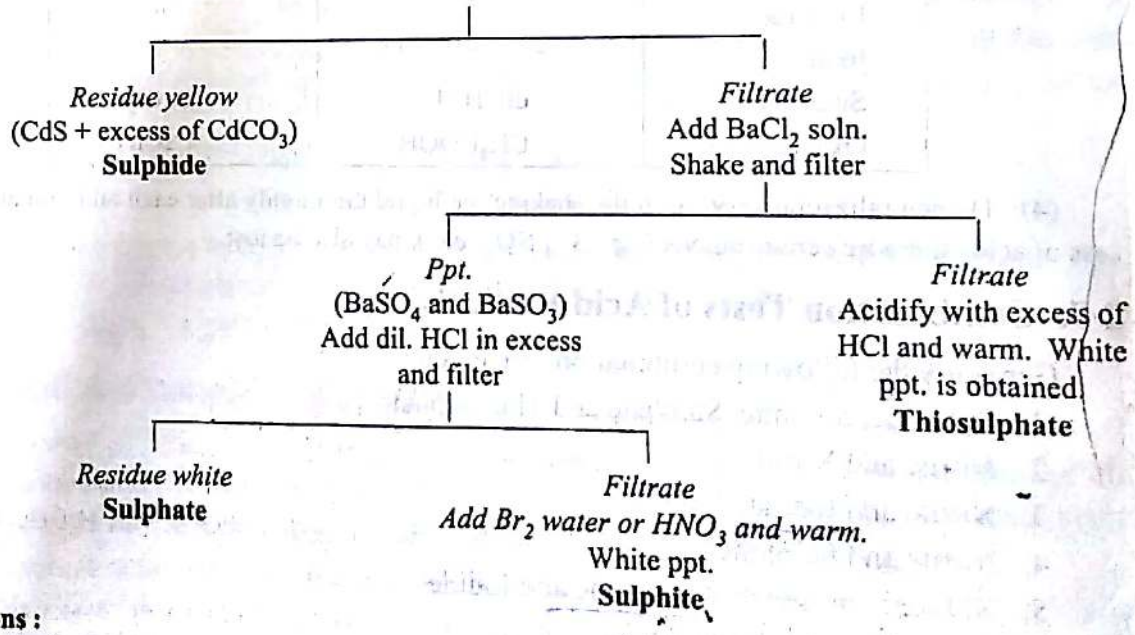
$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + SO_2\uparrow + H_2O$$
$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2\uparrow + S\downarrow + H_2O$$

Finally in presence of S^{2-}, the test for SO_3^{2-} with acidified $K_2Cr_2O_7$ can not be used (H_2S also reduces acidified $K_2Cr_2O_7$ to green chromium salt). Similarly, detection of SO_4^{2-} is difficult in presence of $S_2O_3^{2-}$ or mixture of S^{2-} and SO_3^{2-}. In both cases, a white ppt. of sulphur is formed which being insoluble in acids, it may be mistaken for $BaSO_4$.

Procedure of analysis

The systematic analysis of mixture of S^{2-}, $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-}, described in detail below, is based on (*a*) precipitation of S^{2-} by the action of $CdCO_3$, when SO_3^{2-}, SO_4^{2-} and $S_2O_3^{2-}$ remain in solution ; (*b*) precipitation of SO_3^{2-} and SO_4^{2-} by $BaCl_2$ (or $SrCl_2$) or $Sr(NO_3)_2$, which does not precipitate $S_2O_3^{2-}$; (*c*) the fact that $BaSO_4$ (or $SrSO_4$) is almost insoluble while $BaSO_3$ (or $SrSO_3$) is soluble in dilute acids.

Take the sodium carbonate extract and add excess of freshly prepared $CdCO_3$, shake well and filter.



Reactions :

$$Na_2S + CdCO_3 \longrightarrow CdS\downarrow + Na_2CO_3$$

On addition of $BaCl_2$, SO_3^{2-} and SO_4^{2-} both are precipitated but HCl dissolves $BaSO_3$

1. $$Na_2SO_3 + BaCl_2 \longrightarrow BaSO_3\downarrow + 2NaCl$$
2. $$Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4\downarrow + 2NaCl$$

Br_2 water converts SO_3^{2-} to SO_4^{2-} on boiling

$$Br_2 + H_2O \longrightarrow 2HBr + [O]$$
$$BaSO_3 + [O] \longrightarrow BaSO_4\downarrow$$

(*i*) **Thiosulphate.** Boil the mixture with water and filter. Cool the filtrate and add to it a few drops of ferric chloride solution. Dark violet colour appears which fades slowly.

Analysis of Acid Radicals

(a) mix + 2ml dil H_2SO_4

Radicals	Test (Procedure)	Observation
1. Carbonate (CO_3^{2-})	Add 2ml of dil H_2SO_4 to cmpⁿ mix in a test tube.	Effervescence with evolution of colourless gas. (Carbonate may be present)
	→ Pass the gas into lime water	lime water turns milky
	→ When passed in excess	→ milky colour disappears.
2. Nitrite (NO_2^-)	Add 2ml of dil H_2SO_4 in mix.	Reddish brown fumes in cold
	→ Mix dil H_2SO_4 + fresh starch solⁿ + KI solⁿ (fresh)	→ Blue colour
3. Sulphide (S^{2-})	Add 2ml of dil H_2SO_4 in mixture & heat it	Colourless gas with smell of rotten eggs.
	→ Paper dipped in lead acetate solution, when exposed to gas evolved	→ B Paper turns Black. Confirmation by Na_2CO_3 extract test
4. Sulphite (SO_3^{2-})	Add 2ml of dil H_2SO_4 in mixture & heat it	Colourless gas with choking smell of Sulphur
	→ Exposed the filter paper dipped in Acidified dichromate solution to the gas evolved	→ filter paper turns green. Confirmation by Na_2CO_3 extract
	→ Put 4-5 drops of mixture with dil H_2SO_4 in $KMnO_4$ solⁿ	→ decolourise the $KMnO_4$

Radical	Procedure	Observations
Thiosulphate ($S_2O_3^{2-}$)	Add 2ml of Mixture in 2ml of dil H_2SO_4 & heat it	White or yellowish white turbidity appears. Confirmation by Na_2CO_3 extract.
Acetate	Add 2ml of Mixture in 2ml of dil H_2SO_4 & heat it	→ NO fumes (Smells like vinegar)
	→ Aqueous soln of mixture + few drops of Neutral $FeCl_3$ solution	→ Blood red colouration (Colour dissappears on addition of Acid)
Chloride	Add 2ml of Conc^n H_2SO_4 in Mixture warm gently	Colourless pungent gas comes out.
	→ Bring a rod dipped in Conc. NH_4OH near the mouth of test tube	Dense fumes
	→ 1part mixture + 3 times $K_2Cr_2O_7$ + Conc. H_2SO_4 + heat, then pass the vapours into dil NaOH	→ Dark red vapours of Chromyl Chloride are evolved → NaOH soln becomes yellow.
	then Add CH_3COOH & Lead Acetate to the yellow soln.	→ yellow ppt. obtained which is insoluble in Alkalihydroxides & dil HNO_3 but insoluble in CH_3COOH & dil NH_4OH
Bromide	Add 2ml of Conc. H_2SO_4 in Mixture & heat gently	Reddish brown vapours.
	→ Normal Mixture + dil HNO_3 + heat, filter the solution & to the filtrate Add $AgNO_3$ soln	→ Pale yellow ppt. sparingly soluble in NH_4OH

Radicals	Procedure	Observation
Iodide (I^-)	Add 2ml of conc. H_2SO_4 in mixtures warm gently	Violet pungent vapours evolved confirmation by Na_2CO_3 extract.
Nitrate (NO_3^-)	Add 2ml of conc. H_2SO_4 in mixture & warm gently Ring test- 2ml of Na_2CO_3 extract Acidify with dil H_2SO_4 & add 4ml of conc. H_2SO_4 slowly & mix the two liquids ~~brown~~ thoroughly cool the test tube under the stream of water, then add freshly prepared $FeSO_4$ sol^n slowly from the side of the test tube Allowed to stand for 3-minutes.	Light brown gas evolved (NO_3^- may be present) A sharp brown ring will be formed At the junction of two layer.