
UNIT 4 DETECTION OF THE ANIONS

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4.1 INTRODUCTION

You know that the qualitative analysis involves the detection of the anions and the cations present in an inorganic mixture. Sometimes the knowledge of anions present in a mixture provides important clues about the cations which may be present in a mixture and the scheme of analysis to be followed. Therefore, it is desirable to first detect the presence of anions and after that the cations. In this unit, we will discuss the scheme of detection of anions which will be followed by the scheme of analysis of cations in Units 5 and 6.

Objectives

After studying this unit, you should be able to:

- identify anions present in a mixture,
- describe tests for various anions,

- explain the chemistry of various tests for anions,
- prepare water extract and sodium carbonate extract,
- perform tests for identification of anions present in a mixture,
- remove interfering anions from the mixture, and
- perform tests for identifying special combinations of anions.

4.2 CLASSIFICATION OF THE ANIONS

For the systematic identification of the anions present in any mixture, the anions are divided into following three classes:

4.2.1 Anions of Class I

The anions of Class I evolve gases or vapours on treatment with dil. HCl or dil. H_2SO_4 . These anions are carbonate, sulphite, sulphide, thiosulphate, nitrite and acetate, which are the anions of weak acids.

4.2.2 Anions of Class II

The anions of Class II evolve gases or vapours on treatment with conc. HCl or Conc. H_2SO_4 . These anions are fluoride, chloride, bromide, iodide, nitrate and oxalate.

4.2.3 Anions of Class III

The anions of this class do not evolve any gas on treatment with acids. These are identified by formation of precipitate on treatment with certain reagents. Sulphate, borate and phosphate ions are the anions of Class III.

Here we would like to emphasise that unlike scheme of classification of cations, the scheme of classification of anions is not a rigid one since some of the anions belong to more than one of the classes, e.g., acetate. Also, it is not always necessary to test for the presence of anions of Class I before testing for the presence of anions of Class II or Class III in any mixture.

4.3 PRELIMINARY TESTS FOR THE ANIONS

In this unit the tests for all these anions will be systematically discussed. We shall first discuss the preliminary tests for detecting the presence of anions of Class I and Class II, which will be followed by their confirmatory tests. As there are no preliminary tests for the anions of Class III only their confirmatory tests will be discussed.

4.3.1 Preliminary Tests for the Anions of Class I

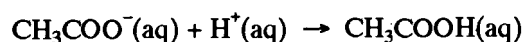
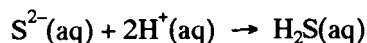
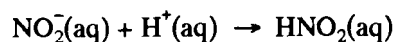
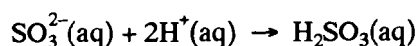
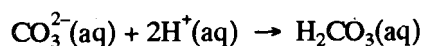
Take about 0.2 g of dry mixture in a test tube. Add 2 cm^3 of dilute hydrochloric or sulphuric acid. If a gas is evolved, note its colour and odour and draw inference with the help of Table 4.1. Heat the test tube if necessary. If no gas is evolved, anions of this class are absent in the mixture.

Table 4.1 : Preliminary Tests for the Anions of Class I

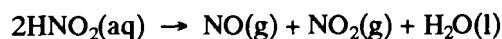
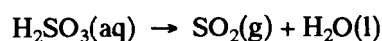
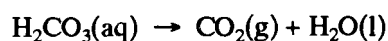
Sl. No.	Observation	Inference	Explanation/ Reaction
1.	Colourless gas evolved with brisk effervescence. On passing the gas in lime water, it turns milky.	CO_3^{2-} may be present	$\text{CO}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ $\text{Ca}(\text{OH})_2(\text{aq}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{l})$

Sl. No.	Observation	Inference	Explanation / Reactopm
2.	Colourless, suffocating gas with smell of burning sulphur; the gas turns acidified $K_2Cr_2O_7$ paper green.	SO_3^{2-} may be present	$SO_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g)$ $Cr_2O_7^{2-}(aq) + 2H^+(aq) + 3SO_2(g) \rightarrow$ $2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + H_2O(l)$ (green)
3.	Colourless, suffocating gas with smell of burning sulphur and there is a deposit of sulphur in the test tube. The gas turns acidified $K_2Cr_2O_7$ paper green.	$S_2O_3^{2-}$ may be present	$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g) + S(s)$
4.	Colourless gas with smell of rotten eggs, turns moistened lead acetate paper black.	S^{2-} may be present	$S^{2-}(aq) + 2H^+(aq) \rightarrow H_2S(g)$ $Pb^{2+}(aq) + H_2S(g) \rightarrow PbS(s) + 2H^+(aq)$ (black)
5.	Light brown gas which turns KI-starch paper blue.	NO_2^- may be present	$2NO_2^-(aq) + 2H^+(aq) \rightarrow H_2O(l) + NO(g) + NO_2(g)$
6.	Colourless vapours with smell of vinegar on warming the test tube.	CH_3COO^- may be present	$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(g)$

When salts of the anions of Class I are treated with strong, non-oxidising acids, corresponding acids are generated in the solution.



Out of these H_2CO_3 , H_2SO_3 and HNO_2 are thermally unstable and decompose into gaseous products, whereas H_2S and CH_3COOH are evolved as vapours on warming:



4.3.2 Preliminary Tests for the Anions of Class II

Take 0.2-0.3 g of the mixture in a dry test tube and add 2-3 cm³ of conc. sulphuric acid dropwise. Observe the reaction at room temperature and then warm the test tube gently. If no gas or vapours are evolved, the anions of this class are absent. Draw inference with the help of Table 4.2.

Table 4.2 : Preliminary Tests for the Anions of Class II

Sl. No.	Observation	Inference	Explanation/Reaction
1.	Colourless, pungent smelling gas is evolved, which gives white dense fumes of NH_4Cl when a glass rod dipped in aqueous ammonia is placed in the evolved gas.	Cl^- may be present	$Cl^-(aq) + H^+(aq) \rightarrow HCl(g)$ $HCl(g) + NH_3(g) \rightarrow NH_4Cl(g)$

Sl. No.	Observation	Inference	Explanation/Reaction
2.	Reddish brown gas is evolved and the solution in the test tube acquires a yellow-red colour.	Br^- may be present	$\text{Br}^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 3\text{SO}_4^{2-}(\text{aq}) \rightarrow 2\text{HSO}_4^-(\text{aq}) + \text{SO}_2(\text{g}) + \text{Br}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
3.	Violet vapours of I_2 are evolved, which turn the moist starch paper blue.	I^- may be present	$2\text{I}^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 3\text{SO}_4^{2-}(\text{aq}) \rightarrow 2\text{HSO}_4^-(\text{aq}) + \text{SO}_2(\text{g}) + \text{I}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
4.	Oily drops inside the test tube and the pungent smelling gas leaves a white deposit on a moistened glass rod.	F^- may be present	$2\text{F}^-(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{HF}(\text{g})$
5.	Pungent smelling, brown fumes of NO_2 are evolved. The evolution of NO_2 increases on heating the reaction mixture with copper turnings.	NO_3^- may be present	$\begin{aligned} \text{NO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) &\rightarrow \text{HNO}_3(\text{aq}) \\ 4\text{HNO}_3(\text{aq}) &\rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \\ \text{Cu}(\text{s}) + 4\text{HNO}_3(\text{aq}) &\rightarrow \text{Cu}(\text{NO}_3)_2(\text{aq}) + 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \end{aligned}$
6.	Colourless, odourless gas is evolved which turns lime water milky and burns with a blue flame	$\text{C}_2\text{O}_4^{2-}$ may be present	$\begin{aligned} \text{C}_2\text{O}_4^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) &\rightarrow \text{CO}(\text{g}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \\ \text{Ca}(\text{OH})_2(\text{aq}) + \text{CO}_2(\text{g}) &\rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) \\ \text{CO}(\text{g}) + \text{O}_2(\text{g}) &\rightarrow \text{CO}_2(\text{g}) \end{aligned}$

4.4 PREPARATION OF SOLUTION FOR IDENTIFICATION OF THE ANIONS

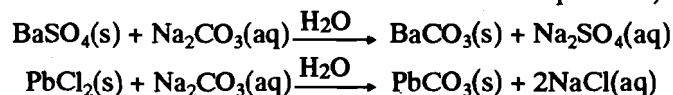
The preliminary tests described in the preceding section do not always offer very conclusive evidence for the presence of anions in a mixture. Therefore, further tests have to be performed for confirmation of those anions which are indicated by the preliminary tests and for the detection and confirmation of the anions of Class III which have no preliminary tests. These tests are called confirmatory tests and are performed on the solution of anions which is prepared as described below.

4.4.1 Preparation of Water Extract

All common acetates, nitrites, nitrates and thiosulphates are soluble in water. Confirmatory tests for these anions can be performed with the water extract of the mixture. Water extract can be prepared by boiling 1-2 g of the mixture with 10-15 cm³ of distilled water in a boiling tube for a minute or two. Residue, if any, is filtered. The filtrate is called **water extract (W.E.)**.

4.4.2 Preparation of Sodium Carbonate Extract

If the mixture is found to be partially or wholly insoluble in water, it is boiled with saturated sodium carbonate solution. This treatment converts the anions present in mixture into soluble sodium salts as a result of double decomposition, e.g.,



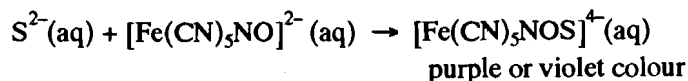
For preparing sodium carbonate extract, take 0.5-1.0 g of powdered mixture, 1.0-2.0 g of sodium carbonate and 5-10 cm³ of distilled water in a boiling tube or a 50 ml beaker. Heat with stirring for 5-10 minutes. Cool the contents and filter. The filtrate is called sodium carbonate extract (S.E.). This extract is used for confirming the presence of most anions except for carbonate since sodium carbonate has been added during its preparation.

4.5 CONFIRMATORY TESTS FOR THE ANIONS

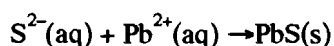
After preparation of the water extract or the sodium carbonate extract, the following tests are performed to confirm the presence of various anions in the mixture.

4.5.1 Tests for the Sulphide Ions

1. Take 1 cm³ of sodium carbonate extract in a test tube and add 1 – 2 cm³ of sodium nitroprusside solution. A purple or violet colour confirms sulphide ions:



2. Take 1 – 2 cm³ of S.E. in a test tube, acidify it with acetic acid and boil to remove CO₂. Then add 1–2 cm³ of lead acetate solution. Formation of black precipitate confirms sulphide ions:



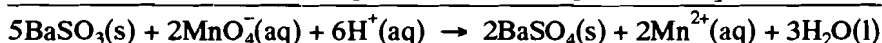
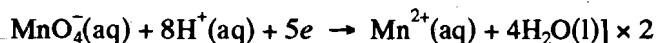
4.5.2 Tests for the Sulphite Ions

Take 2–3 cm³ of S.E. and add 2–3 cm³ of BaCl₂ solution to it. A white precipitate may appear due to the presence of SO₃²⁻, SO₄²⁻ or excess of CO₃²⁻ ions present in the solution. Filter the precipitate and divide into three parts.

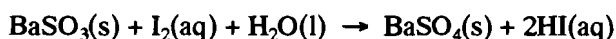
1. To the first part, add dil. HCl. Evolution of SO₂ gas which turns acidified dichromate paper green confirms the presence of SO₃²⁻ ions:



2. To the second part, add a few drops of KMnO₄ solution and acidify with dil. H₂SO₄. If the pink colour of KMnO₄ is discharged, the presence of SO₃²⁻ ions is confirmed:

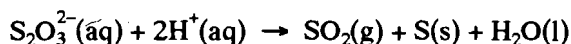


3. To the third part, add I₂ solution. If colour of iodine is discharged, SO₃²⁻ is confirmed:

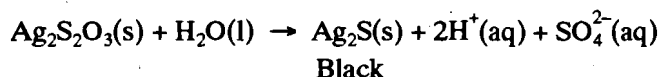
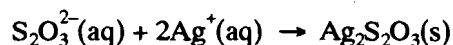


4.5.3 Tests for the Thiosulphate Ions

1. Take 1–2 cm³ of S.E. in a test tube and acidify with dil. H₂SO₄. Evolution of SO₂ accompanied by a yellow precipitate of sulphur confirms the presence of thiosulphate ions:

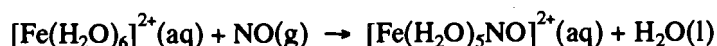
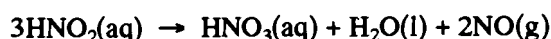


2. Take 1 – 2 cm³ of S.E. in a test tube and acidify with acetic acid. Add 1 cm³ of AgNO₃ solution. Formation of white precipitate which turns yellow, orange–brown and finally black in quick succession confirms the presence of thiosulphate ions:

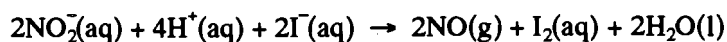


4.5.4 Tests for the Nitrite Ions

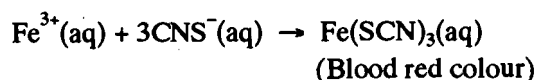
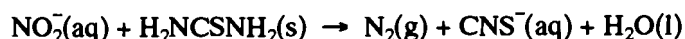
1. Take 5 drops of W.E. in a test tube. Dilute with 5 drops of distilled water. Add 5 M acetic acid until the solution is just acidic. Cool the test tube in a cold water bath. Add 2-3 drops of freshly prepared 0.2 M FeSO_4 solution to the cooled solution. Appearance of a brown colour throughout the solution confirms the presence of nitrite ions:



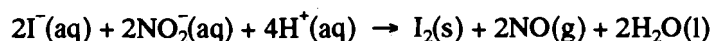
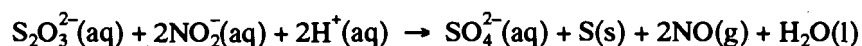
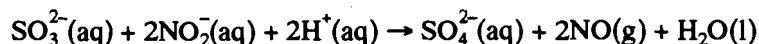
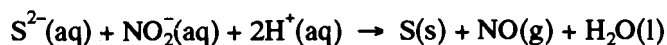
2. To 1 cm^3 of W.E. add 5 drops of KI solution, 1 cm^3 of starch solution and 1 cm^3 of dil. H_2SO_4 . Appearance of a deep blue colour confirms the presence of nitrite ions:



3. Take 5 drops of W.E in a test tube, acidify with 6 M acetic acid. Add a pinch of thiourea and stir well. Add 2 drops of FeCl_3 solution. A blood red colour confirms nitrite ions:

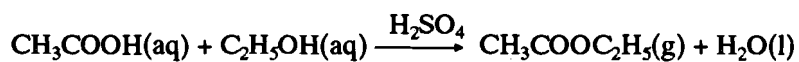
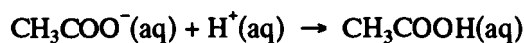


You should note that the nitrite ion is a moderately strong oxidising agent in acidic medium. It oxidises S^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$ and I^- ions to S, SO_4^{2-} , $\text{SO}_4^{2-} + \text{S}$, and I_2 respectively. Therefore, these anions cannot be present if NO_2^- ions are present in the mixture.



4.5.5 Tests for the Acetate Ions

1. Take 1 g of the mixture, 1 cm^3 of conc. H_2SO_4 and 2-3 cm^3 of rectified spirit in a test tube. Warm the contents gently for several minutes. Ethyl acetate is formed, which can be recognised by its pleasant, fruity odour. This confirms the presence of acetate ions in the mixture:



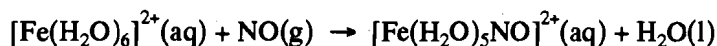
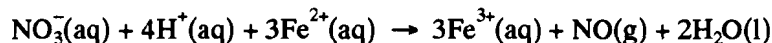
It is preferable to use iso-amyl alcohol, if easily available in the laboratory, because the banana like odour of the resulting iso-amyl acetate is more readily distinguished.

2. Take 0.5 cm^3 of W.E. in a test tube. Add $\text{Ba}(\text{NO}_3)_2$ solution to precipitate SO_4^{2-} and PO_4^{3-} ions if present. Filter the precipitate and discard it. Now add 0.5 cm^3

of 0.1 M $\text{La}(\text{NO}_3)_3$ solution and add 0.01 M I_2 solution dropwise till the colour of I_2 persists. Wait for a minute and add 1 drop of 1 M aqueous ammonia. If a blue or blue-brown ring is developed around the ammonia drop within a few minutes, presence of acetate ions is confirmed. The ring probably develops due to the adsorption of iodine by basic lanthanum acetate.

4.5.6 Tests for the Nitrate Ions

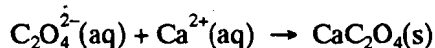
Take 2 cm³ W.E. in a test tube. Add 4 cm³ concentrated sulphuric acid, mix the two liquids thoroughly and cool the mixture under a stream of cold water from the tap. Pour 3 cm³ of saturated solution of FeSO_4 slowly down the side of the test tube so that it forms a separate layer on top of the solution in the test tube. A brown ring will be formed at the zone of contact of the two liquids:



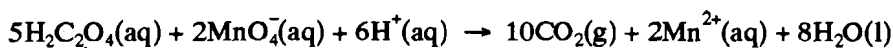
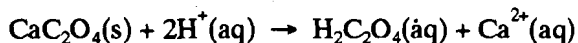
This test for nitrate ion is based on its ability to oxidise Fe^{2+} to Fe^{3+} in acidic solution with the production of NO gas. Since NO is more soluble in water at low temperature, in well cooled solution it reacts with excess Fe^{2+} present in solution to form brown nitrosyliron(II) complex ion, $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$. Nitrite, bromide and iodide ions interfere in this test.

4.5.7 Tests for the Oxalate Ions

Take 2–3 cm³ of S.E. in a test tube. Acidify with acetic acid. Add aqueous ammonia till a smell of ammonia persists (you may test with litmus paper). Heat for 2 minutes to remove excess of ammonia. Add CaCl_2 solution. Formation of a white precipitate indicates the presence of oxalate ions.

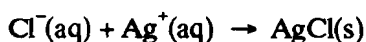


Filter the precipitate and dissolve it in dil. H_2SO_4 . Warm the solution and add 1 cm³ of KMnO_4 solution. If pink colour is discharged with the evolution of CO_2 gas, the presence of oxalate ions is confirmed.

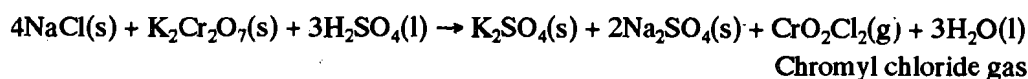


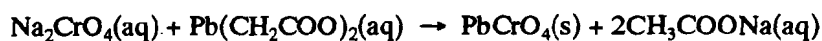
4.5.8 Tests for the Chloride Ions

1. Acidify 2–3 cm³ of S.E. with dil. HNO_3 . Boil off CO_2 . Then add AgNO_3 solution. Formation of a curdy white precipitate, which is soluble in aqueous ammonia, confirms the presence of chloride ions in the mixture.



2. Heat 0.5 g of dry mixture with 0.5 g of $\text{K}_2\text{Cr}_2\text{O}_7$ and 2 cm³ of conc. H_2SO_4 in a dry test tube, red vapours of chromyl chloride will be evolved. Pass the vapours in dil. NaOH solution, a yellow solution will be obtained. Acidify the solution with acetic acid and then add lead acetate solution. Formation of a yellow precipitate of lead chromate, which is soluble in NaOH , confirms the presence of chloride ions.

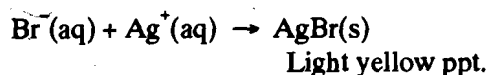




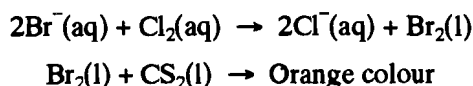
Due to the formation of chromyl chloride gas, this test is called **chromyl chloride test**. The test fails if the mixture contains chlorides of Hg^{2+} , Sn^{2+} , Pb^{2+} or Ag^+ .

4.5.9 Tests for the Bromide Ions

1. Acidify 2–3 cm³ of S.E. with dil. HNO_3 and boil off CO_2 . Add AgNO_3 solution. Formation of a light yellow precipitate which is partially soluble in aqueous ammonia solution, confirms the presence of bromide ions:

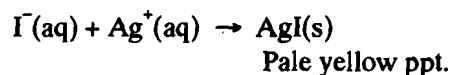


2. Take 2 cm³ of S.E., acidify it with dil. HCl and boil off CO_2 . Add 2 cm³ of carbon disulphide, dichloromethane or carbon tetrachloride. Then add chlorine water dropwise and shake. Bromide ions are oxidised to bromine, which imparts an orange colour to the organic layer. This confirms the presence of bromide ions in the mixture.

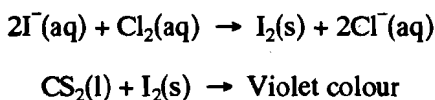


4.5.10 Tests for the Iodide Ions

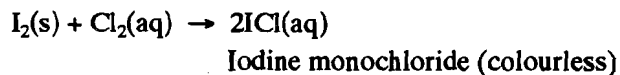
1. Acidify 2–3 cm³ of S.E. with dil. HNO_3 and boil off CO_2 . Add AgNO_3 solution. Formation of a pale yellow precipitate insoluble in aqueous ammonia confirms the presence of iodide ions in the mixture.



2. Take 2 cm³ of S.E. in a test tube. Acidify it with dil. HCl and boil off CO_2 . Add 2 cm³ of carbon disulphide, dichloromethane or carbon tetrachloride. Then add chlorine water dropwise and shake. Iodide ions are oxidised to iodine, which imparts a violet colour to the organic layer.

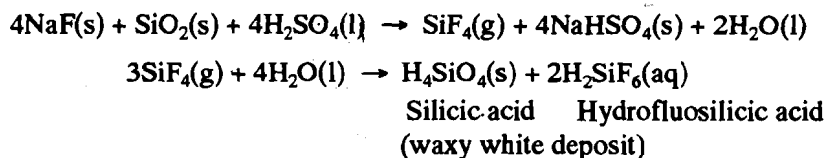


The violet colour disappears on addition of excess of chlorine water. This confirms the presence of iodide ions in the mixture:

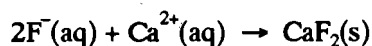


4.5.11 Tests for the Fluoride Ions

1. Take 0.5 g of powdered mixture, an equal amount of sand and 2 cm³ of conc. H_2SO_4 in a dry test tube. Heat the test tube, vapours of SiF_4 will be given off. Hold a moistened glass rod in the vapours. Formation of a waxy white deposit on the glass rod, confirms the presence of fluoride ions in the mixture.



2. Take 2 cm³ of S.E. in a test tube. Acidify with acetic acid and boil off CO₂. Add CaCl₂ solution. A white precipitate of CaF₂ may be formed.

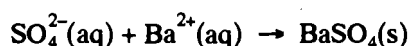


Filter the precipitate and dissolve it in dil. H₂SO₄. Warm and add a few drops of KMnO₄. Pink colour of KMnO₄ is not discharged (difference from oxalate). This confirms the presence of fluoride ions in the mixture.

So far we have discussed the confirmatory tests for the anions of Class I and II which are indicated by preliminary tests with sulphuric acid. Now, we shall discuss the confirmatory tests for the anions of Class III, i.e., sulphate, phosphate and borate ions, which are not indicated by preliminary tests

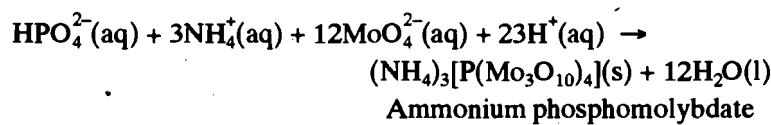
4.5.12 Test for the Sulphate Ions

Take 2–3 cm³ of S.E. in a test tube. Acidify it with dil. HCl and boil off CO₂. Add BaCl₂ solution. Appearance of a white precipitate, which is insoluble in conc. HCl and conc. HNO₃, confirms the presence of sulphate ions.

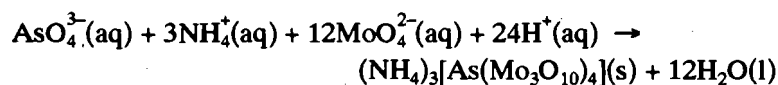


4.5.13 Tests for the Phosphate Ions

Take 1–2 cm³ of S.E. in a test tube, acidify it with 6 M HNO₃ and then add 2–3 cm³ of ammonium molybdate solution. Warm the solution gently to 40° C. A canary yellow precipitate is slowly formed, which is soluble in ammonium acetate, aqueous ammonia and caustic alkali. This confirms the presence of phosphate ions.



Arsenate ion interferes in this test, as it also produces a similar yellow precipitate of ammonium arsenomolybdate.

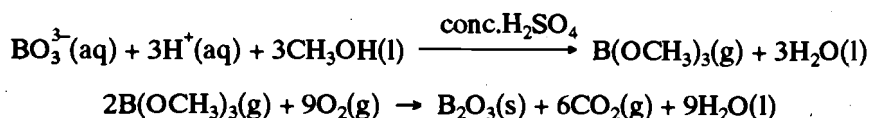


Both ammonium phosphomolybdate and ammonium arsenomolybdate dissolve on boiling with ammonium acetate solution, but only the latter yields a white precipitate on cooling. The presence of phosphate ions in the mixture is further confirmed by testing in the filtrate of Group II after precipitation of As₂S₃ or As₂S₅ as follows:

Take 2–3 cm³ of the filtrate in a china dish and boil off H₂S from it. Add 1 cm³ of 6 M HNO₃ and 1 cm³ of ammonium molybdate solution. Warm and wait for 2 minutes. If a yellow precipitate is formed, it confirms the presence of phosphate ions in the mixture.

4.5.14 Test for the Borate Ions

The test for borate ions is based on the reaction of borate ions with methanol in presence of concentrated sulphuric acid, which acts as a dehydrating agent. On heating volatile methyl borate is formed, which burns with a green edged flame. This confirms the presence of borate ions:



Isolate the vapours from the mixture before burning otherwise Ba^{2+} and Cu^{2+} salts interfere because these salts also impart a green colour to the alcohol flame.

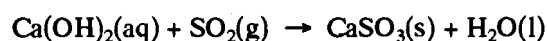
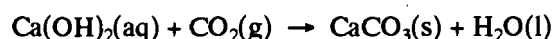
Take 0.5 g of the mixture, 1 cm^3 of concentrated sulphuric acid and 1 cm^3 of methanol or ethanol in a china dish. Invert a funnel in the dish. Place the dish on a wire gauze and heat gently. Allow the vapours to pass out off the stem of the funnel. Burn the vapours. A green coloured flame confirms borate ions in the mixture.

4.6 SPECIAL TESTS FOR THE MIXTURES OF THE ANIONS

Confirmatory tests for some anions discussed in the preceding section fail in presence of certain other anions in the mixture. For example, the silver nitrate test for the bromide ions fails if iodide ions are also present in the mixture, because both form a yellow precipitate with silver nitrate. In this section, we shall discuss the confirmatory tests for anions which can be performed in presence of other anions also.

4.6.1 Test for Carbonate Ions in Presence of Sulphite and/or Thiosulphate Ions

Sulphites and thiosulphates on treatment with dil. H_2SO_4 produce SO_2 , which like CO_2 turns lime water turbid or milky. Hence, it cannot be inferred whether the turbidity is due to carbonate, sulphite or thiosulphate.



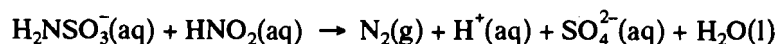
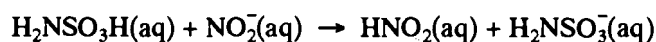
In order to test for carbonate ions in presence of sulphite or thiosulphate ions, take 0.5 g of mixture and 0.5 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in a test tube. Add 2–3 cm^3 of dil. H_2SO_4 . Heat the test tube and pass the evolved gas through lime water. If lime water turns milky, it confirms the presence of carbonate ions in the mixture. SO_2 liberated by reaction of sulphite and/or thiosulphate with dil. H_2SO_4 is trapped by $\text{K}_2\text{Cr}_2\text{O}_7$ in the test tube, which turns green.



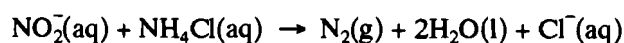
4.6.2 Tests for Nitrate Ions in Presence of Nitrite Ions

In presence of nitrite, nitrate cannot be tested either by heating with conc. H_2SO_4 or by the ring test because both liberate NO_2 . Therefore, nitrite must be destroyed completely before testing for the nitrate. Nitrite ions can be destroyed by any one of the following methods:

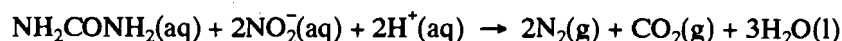
1. Add sulphamic acid, $\text{H}_2\text{NSO}_3\text{H}$, to the water extract containing NO_2^- and NO_3^- ions. Acidify the solution with dilute H_2SO_4 . Nitrite will be decomposed and nitrogen gas will be evolved.



2. Take 2–3 cm^3 of water extract, add 1 g solid NH_4Cl and boil till effervescence ceases.

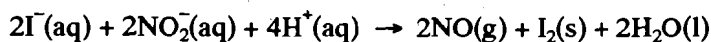
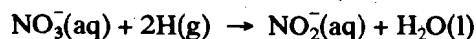


3. Take 2–3 cm^3 of water extract, add urea and acidify with dil. H_2SO_4 . Boil the solution till evolution of gases ceases.



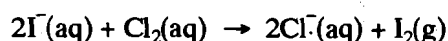
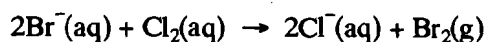
Now divide the nitrite free solution thus obtained in two parts.

- Perform ring test with one part to confirm the presence of nitrate ions.
- Acidify the other part with dil. H_2SO_4 . Add a little KI and 1 cm^3 starch solution. Absence of any blue colour indicates the complete removal of nitrite ions. Now add a piece of granulated zinc to the solution. Appearance of a blue colour confirms the presence of nitrate ions:



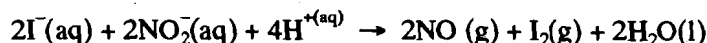
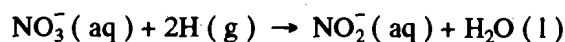
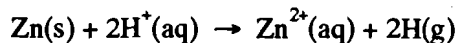
4.6.3 Tests for Nitrate Ions in Presence of Bromide and/or Iodide Ions

- Bromide and iodide interfere in the ring test of nitrate because of the colour of liberated bromine and iodine. In order to identify nitrate in presence of iodide and/or bromide, the interfering halide should be expelled before performing the ring test. This can be done by boiling $2-3\text{ cm}^3$ of water extract or sodium carbonate extract with excess of chlorine water in a china dish, till no more vapours of Br_2 or I_2 evolve:



Now perform the ring test on the halide free solution to identify the nitrate ion in the mixture.

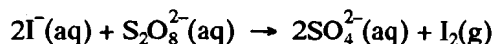
- Alternatively, take $2-3\text{ cm}^3$ of water extract in a test tube. Acidify with dil. H_2SO_4 . Now add 1 cm^3 of KI solution, 1 cm^3 of starch solution and a few granules of zinc. Appearance of a blue colour confirms the presence of nitrate ions in the mixture.



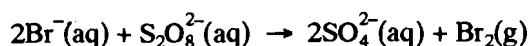
4.6.4 Tests for Chloride, Bromide and Iodide Ions in Presence of Each Other

As you know that chloride, bromide and iodide ions react with AgNO_3 solution to form a precipitate, special tests are required to identify if more than one of them are present in the mixture. These anions can be detected in presence of one another by any one of the following methods:

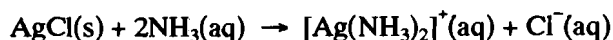
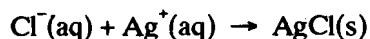
- Acidify $2-3\text{ cm}^3$ of S.E. with excess of dil. H_2SO_4 in a china dish. Add 0.5 g of potassium persulphate and heat gently. Add distilled water if necessary to prevent dryness. Evolution of violet vapours of I_2 will confirm the presence of I^- ions.



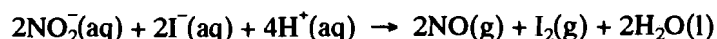
Boil till evolution of I_2 ceases. If the solution after elimination of I_2 is brown, it indicates the presence of Br^- ions. Continue boiling, brown vapours of Br_2 will be evolved:



Add more $\text{K}_2\text{S}_2\text{O}_8$ if required. Continue boiling till the residual solution becomes colourless. Cool the solution, add dil. HNO_3 and AgNO_3 solution. A curdy white precipitate soluble in ammonia confirms the presence of Cl^- ions in the mixture:

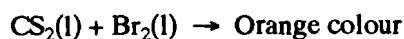
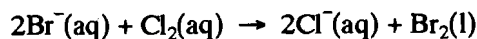


2. Acidify 2–3 cm^3 of S.E. with dil. H_2SO_4 in a china dish. Boil off CO_2 . Add solid sodium nitrite and boil. Evolution of violet vapours of I_2 confirms the presence of iodide ions:



Add distilled water if necessary to prevent dryness. Continue boiling till all iodine is expelled. Cool the solution and divide into 2 parts.

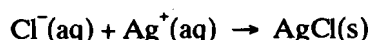
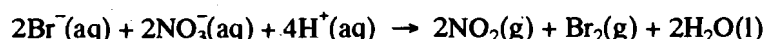
To 1st part add 1 cm^3 CS_2 (or CH_2Cl_2 or CCl_4), 2 cm^3 chlorine water and shake. Appearance of an orange colour in organic layer confirms the presence of bromide ions:



If Br^- is present, boil the 2nd part with 1 cm^3 of conc. HNO_3 to expel Br_2 gas.

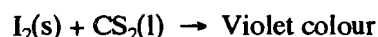
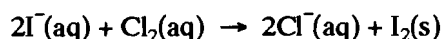
This treatment can be avoided if Br^- ion is absent. Then add AgNO_3 solution.

Formation of a curdy white precipitate confirms the presence of Cl^- ions:

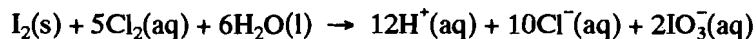


4.6.5 Tests for Bromide and Iodide Ions in Presence of Each Other

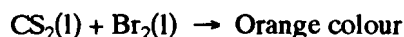
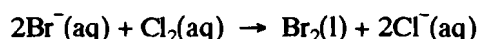
Take 2–3 cm^3 of S.E. in a test tube and acidify with dil. HCl . Add 2 cm^3 of CS_2 (or CH_2Cl_2 or CCl_4) and chlorine water dropwise with shaking. Appearance of violet colour in organic layer confirms iodide ions in the mixture.



Continue adding chlorine water and shaking till violet colour disappears due to the formation of colourless iodic acid:

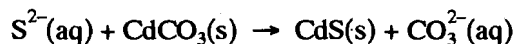


Continue adding chlorine water and shaking. If the organic layer becomes orange, bromide is confirmed:



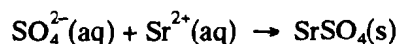
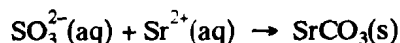
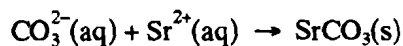
4.6.6 Tests for Sulphide, Sulphite, Thiosulphate and Sulphate Ions in Presence of Each Another

Take 2–3 cm^3 of S.E. containing the above anions in a test tube. Add solid CdCO_3 . If a yellow precipitate is formed, sulphide ion is confirmed.



Filter the precipitate and add $\text{Sr}(\text{NO}_3)_2$ solution. A white precipitate may be

obtained due to the formation of SrCO_3 , SrSO_3 and SrSO_4 .



SrS_2O_3 being soluble will remain in the solution. Filter the precipitate and proceed as follows:

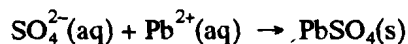
Filtrate may contain SrS_2O_3 . Add a few drops of AgNO_3 solution. A white precipitate turning yellow, orange, brown and finally black confirms thiosulphate.	Residue may contain SrCO_3 , SrSO_3 and SrSO_4 . Add dil. HCl and filter	
$\text{S}_2\text{O}_3^{2-}(\text{aq}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Ag}_2\text{S}_2\text{O}_3(\text{s})$	Filtrate may contain SrSO_3 . Add conc. HNO_3 and heat. Formation of a white ppt. confirms sulphite ions.	White residue of SrSO_4 confirms the presence of sulphate ions
$\text{Ag}_2\text{S}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ag}_2\text{S}(\text{s}) + 2\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ Black	$\text{SrSO}_3(\text{aq}) + \text{O} \rightarrow \text{SrSO}_4(\text{s})$	

4.6.7 Test for Sulphate Ions in the Presence of Fluoride Ions

Since BaF_2 also is insoluble in dil. HCl, the presence of F^- ions interferes with the BaCl_2 test for the SO_4^{2-} ions. But in dilute acetic acid, PbF_2 is soluble whereas PbSO_4 is insoluble. Therefore, the following test is employed for the identification of SO_4^{2-} ions in the presence of F^- ions.

Take 2–3 cm³ of S.E. in a test tube. Acidify with dilute acetic acid and boil off CO_2

Now add lead acetate solution. Formation of a white precipitate confirms the presence of SO_4^{2-} ions in the mixture.

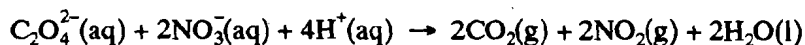


4.7 REMOVAL OF INTERFERING ANIONS

Most of the fluorides, borates, oxalates and phosphates are soluble in dilute strong acids but are insoluble in neutral and basic solutions. Therefore, when aqueous ammonia solution is added to the filtrate of Group II, not only the hydroxides of Al^{3+} , Cr^{3+} and Fe^{3+} precipitate, but the fluorides, borates, oxalate or phosphates of cations of Group III to VI also precipitate from the solution. In this way, these anions interfere in the analysis of cations of Group III to VI. Therefore, fluoride, borate, oxalate and phosphate are known as interfering anions. These anions must be eliminated before proceeding for precipitation of the cations of Group III.

4.7.1 Removal of Oxalate Ions

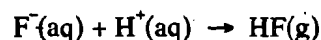
Oxalate ions can be removed by repeatedly evaporating the solid mixture or the filtrate of Group II with concentrated nitric acid to near dryness. This process is repeated several times until the residue gives a negative test for the oxalate ions. Nitric acid oxidises the oxalate ions to CO_2 and water.



Take the filtrate of Group II in a china dish. Boil off H_2S (test with lead acetate paper). Add 2–3 cm³ of conc. HNO_3 and evaporate to near dryness. Do not heat the residue to complete dryness as iron(III) oxide, chromium(III) oxide and aluminium(III) oxide are rendered insoluble. Repeat the process 2–3 times until the residue gives a negative test for oxalate ions. Dissolve the residue in dil. HCl and use the solution for the analysis of cations of Group III–VI.

4.7.2 Removal of Fluoride Ions

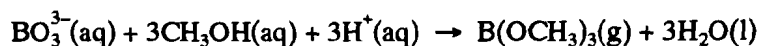
Fluoride ions can be removed by repeatedly evaporating the dry mixture or the filtrate of Group II with conc. HCl in a china dish. Fluoride ions are volatilised off as hydrofluoric acid:



Take the filtrate of Group II in a china dish. Boil off H_2S (test with lead acetate paper). Add 2–3 cm^3 of conc. HCl and evaporate to almost dryness. Repeat the process 2-3 times till fluoride ions are completely eliminated. Extract the residue in dil. HCl and use the solution for the analysis of the cations of Group III-VI.

4.7.3 Removal of Borate Ions

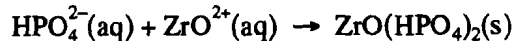
Boil off H_2S from the filtrate of Group II taken in a china dish (test with lead acetate paper). Evaporate to almost dryness. Cool and add 2 cm^3 of conc. HCl and 2 cm^3 of methyl or ethyl alcohol. Alternatively take 0.5 g of the dry mixture in a china dish and add 2 cm^3 of conc. HCl and 2 cm^3 of methyl or ethyl alcohol. Heat on a water bath until nearly dry. Repeat this process a second time. Borate ions are volatilised off as methyl or ethyl borate:



Finally extract the residue in 2–3 cm^3 of dil. HCl and use for the analysis of cations of Group III-VI.

4.7.4 Removal of Phosphate Ions

Removal of phosphate ions is based on the fact that zirconyl phosphate, $\text{ZrO}(\text{HPO}_4)_2$, is precipitated from a solution containing hydrochloric acid not exceeding 1 M concentration.



The precipitate is of variable composition depending on the concentrations of ZrO^{2+} , PO_4^{3-} and H^+ ions. Species like $\text{Zr}(\text{HPO}_4)_2$, ZrPO_4 and $\text{ZrO}(\text{H}_2\text{PO}_4)_2$ may be formed.

Transfer the filtrate of Group II in a china dish and boil off H_2S (test with lead acetate paper). Add a few drops of conc. HNO_3 and adjust the HCl concentration so that it does not exceed 1M. Add 1.0-2.0 g solid NH_4Cl . Then add zirconyl nitrate solution dropwise and stir with a glass rod. Heat on a boiling water bath for 2 minutes. Cool and filter. Add a few more drops of zirconyl nitrate solution to make sure that all the phosphate ions have been precipitated. Use the filtrate for the analysis of cations of Group III-VI.

4.8 SUMMARY

In this unit you learnt the tests for detection and identification of individual anions, which may be present in an inorganic mixture. You also learnt special tests for the mixture of the anions. Certain anions, e.g., the oxalate, fluoride, borate and the phosphate, if present in a mixture, interfere in the scheme of identification of the cations present in the mixture. These anions are called the interfering anions. Therefore, the interfering anions should be identified and then removed before attempting to identify the cations present in the mixture. You also learnt the tests for the identification of the interfering anions and the treatment which should be given to the mixture for the removal of the interfering anions.