

**B. Sc. I YEAR
LAB MANUAL**

LAB MANUAL

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DEPARTMENT OF CHEMISTRY

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INORGANIC CHEMISTRY LAB

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LABORATORY APPARATUS AND OPERATION

A. Common Laboratory Apparatus:

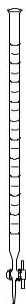
Beakers are useful as a reaction container or to hold liquid or solid samples. They are also used to catch liquids from titrations and filtrates from filtering operations.



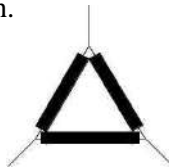
Bunsen Burners are sources of heat.



Burettes are for addition of a precise volume of liquid. The volume of liquid added can be determined to the nearest 0.01 ml. with practice.



Clay Triangles are placed on a ring attached to a ring stand as a support for a funnel, crucible, or evaporating dish.



Droppers are for addition of liquids drop by drop



Erlenmeyer Flasks are useful to contain reactions or to hold liquid samples. They are also useful to catch filtrates.



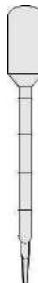
Glass Funnels are for funneling liquids from one container to another or for filtering when equipped with filter paper.



Graduated Cylinders are for measurement of an amount of liquid. The volume of liquid can be estimated to the nearest 0.1 m with practice.



Pipets are used to dispense small quantities of liquids.



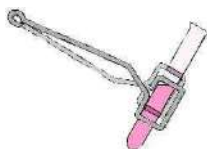
Ring stand with Rings are for holding pieces of glassware in place.



Test Tubes are for holding small samples



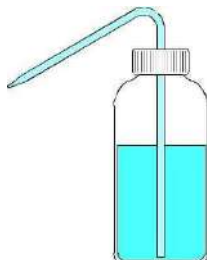
Test tube holders are for holding test tubes when tubes should not be touched



Volumetric Flasks are used to measure precise volumes of liquid or to make precise dilutions.



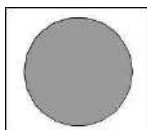
Wash bottles are used for dispensing small quantities of distilled water.



Watch glasses are for holding small samples or for covering beakers or evaporating dishes.

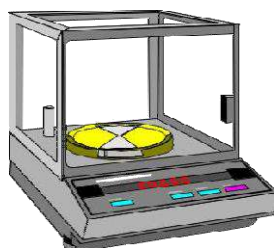


Wire Gauze on a ring supports beakers to be heated by Bunsen burners



B. Laboratory equipment:

Balances are used to determine the mass of a reagent or object.



COMMON LABORATORY REAGENTS

Name	General Description
Acetic acid	An organic acid; is one of the simplest carboxylic acids.
Acetone	An organic compound: simplest example of the ketones
Acetylene	A hydrocarbon and the simplest alkyne; widely used as a fuel and chemical building block
Ammonia	Inorganic; the precursor to most nitrogen-containing compounds; used to make fertilizer.
Ammonium hydroxide	Aqueous ammonia; used in traditional qualitative inorganic analysis
Azobisisobutyron trile	Organic compound; often used as a foamer in plastics and rubber and as a radical initiator
Baeyer's reagent	An alkaline solution of potassium permanganate; used in organic chemistry as a qualitative test for the presence of unsaturation, such as double bonds;
N-Bromosuccinimide	Used in radical substitution and electrophilic addition reactions in organic chemistry
Butanone(methyl ethyl ketone)	Organic compound; similar solvent properties to acetone but has a significantly slower evaporation rate.
Butylated hydroxytoluene	A fat soluble organic compound that is primarily used as an antioxidant food additive
n-Butyllithium	An organolithium reagent; used as a polymerization initiator in the production of elastomers such as polybutadiene or styrene-butadiene-styrene(SBS)
Carbon disulfide	A non-polar solvent; used frequently as a building block in organic chemistry
Carbon	Toxic, and its dissolving power is low; consequently, it has been largely
Tetrachloride	Supersede by deuterated solvents
Carbonyldiimidazole	Often used for the coupling of amino acids for peptide synthesis and as a reagent in organic

	synthesis
Ric ammonium nitrate	An organic compound; used as an oxidising agent in organic synthesis and as a standard oxidant in quantitative analysis
Chloroform	Organic compound; often used as CDCl ₃ (deuterated chloroform) as a solvent for NMR spectroscopy and as a general solvent.
Chromic acid	A strong and corrosive oxidising agent; an intermediate in chromium plating
Chromium trioxide	The acidic anhydride of chromic acid; mainly used in chrome-plating .
Chromium trioxide	The acidic anhydride of chromic acid; mainly used in chrome-plating
Collins reagent	Used to selectively oxidize primary alcohols to an aldehyde
Copper(I) iodide	Useful in a variety of applications ranging from organic synthesis to cloud seeding
Dess-martin periodinane	Chemical reagent used to oxidize primary alcohols to aldehydes and secondary alcohols to ketones
Diborane	The central organic synthesis reagent for hydroboration
Diethyl azodicarboxylate	A valuable reagent but also quite dangerous and explodes upon heating
Diethyl ether	Organic compound; a common laboratory solvent
Dihydropyran	A heterocyclic compound; used as a protecting group for alcohols in organic synthesis.
Diisobutylaluminum hydride	An organoaluminum compound; a reducing agent; converts esters and nitriles to aldehydes
Diisopropyl azodicarboxylate	The diisopropyl ester of azodicarboxylic acid; a reagent in the production of many organic compounds
Dimethyl ether	The simplest ether, a useful precursor to other organic compounds and an aerosol propellant
Dimethylformamide	Organic compound; a common solvent for chemical reactions
Dimethylsulfide	Organosulfur compound; used in petroleum refining and in petrochemical production processes; a reducing agent in ozonolysis reactions.
Dimethyl sulfoxide	An organosulfur compound; an important polar

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	aprotic solvent that dissolves both polar and nonpolar compounds
Dioxane	A heterocyclic organic compound; classified as an ether
Ethanol	A powerful psychoactive drug; used in alcoholic beverages, in thermometers, as a solvent, and as a fuel.
Fehling's reagent	Used to differentiate between water-soluble aldehyde and ketone functional groups
Fentons' reagent	A solution of hydrogen peroxide and an iron catalyst that is used to oxidize contaminants or waste waters.
Formaldehyde	The simplest aldehyde; an important precursor to many other chemical compounds; such as polymers and polyfunctional alcohols
Formic acid	The simplest carboxylic acid; often used as a source of the hydride ion
Grignard reagents	The most common application is for alkylation of aldehydes and ketones;
Hydrazine	It's a good reducing agent and is used in the wolff-kishner reaction for reducing carbonyls to its corresponding alkanes. Used as a foaming agent in preparing polymer foams; also a precursor to polymerization catalysts and pharmaceuticals; also as an oxygen scavenger in power plants.
Hydrazoic acid	Used primarily for preservation of stock solutions, and as a reagent
Hydrochloric acid	A highly corrosive, strong mineral acid with many industrial uses
Hydrofluoric acid	Valued source of fluorine, precursor to numerous pharmaceuticals; highly corrosive
Hydrogen peroxide	Commonly used as a bleach
Imidazole	An organic compound; this aromatic heterocyclic is a diazole and is classified as an alkaloid
Isopropyl alcohol	Simplest example of a secondary alcohol; dissolves a wide range of non-polar compounds
Lime	Used in flue gas desulphurisation in power plants.
Limestone	Used in Flue Gas Desulphurisation in power plants
Manganese dioxide	Used as a pigment and as a precursor to other

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	manganese compounds; used as a reagent in organic synthesis for the oxidation of allylic alcohols
Methyl tert-butyl ether	A gasoline additive; also used in organic chemistry as a relatively inexpensive solvent.
Millon's reagent	An analytical reagent used to detect the presence of soluble proteins
Nitric acid	Highly corrosive and toxic strong acid; used for the production of fertilizers, production of explosives, and as a component of aqua regia
Osmium tetroxide	In organic synthesis, is widely used to oxidise alkenes to the vicinal diols
Oxalyl chloride	Used in organic synthesis for the preparation of acid chlorides from the corresponding carboxylic acids
Palladium(II) acetate	A catalyst for many organic reactions by combining with many common classes of organic compounds to form reactive adduct.
Perchloric acid	A powerful oxidizing agent; readily forms explosive mixtures; mainly used in the production of rocket fuel
Phosphoric acid	A mineral acid with many industrial uses; commonly used in the laboratory preparation of hydrogen halides
Phosphorus	One of the most important phosphorus chlorides; a chlorinating reagent.
Pentachloride	Also used as a dehydrating agent for oximes which turn them into nitriles.
Phosphorus trichloride	Most important of the three phosphorus chlorides; used to manufacture organophosphorus compounds; used to convert primary and secondary alcohols into alkyl chlorides, or carboxylic acids into acyl chlorides.
Phosphoryl chloride	Used to make phosphate esters such as tricresyl phosphate.
Potassium dichromate	A common inorganic chemical reagent, most commonly used as an oxidizing agent in various laboratory and industrial applications
Potassium hydroxide	A strong oxidizing agent; can be used to quantitatively determine the total oxidizable

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	organic material in an aqueous sample. A reagent for the synthesis of organic compounds
Raney nickel	An alternative catalyst for the hydrogenation of vegetable oils; in organic synthesis, used for desulfurization
Silver oxide	Used to prepare other silver compounds; in organic chemistry, used as a mild oxidizing agent.
Silver nitrate	Precursor to many other silver compounds; commonly used in organic chemistry to abstract halides
Sodium amide	Used in the industrial production of indigo, hydrazine, and sodium cyanide; used for the drying of ammonia; used as a strong base in organic chemistry
Sodium azide	Gas-forming component in airbag systems; used in organic synthesis to introduce the azide functional group by displacement of halides
Sodium	A versatile reducing agent; converts ketones and aldehydes to alcohols
Sodium chlorite	In organic synthesis, used for the oxidation of aldehydes to carboxylic acids.
Sodium hydride	A strong base used in organic synthesis.
Sodium hydroxide	Strong base with many industrial uses; in the laboratory, used with acids to produce the corresponding salt, also used as an electrolyte
Sodium nitrite	Used to convert amines into diazo compounds
Sulfuric acid	Strong mineral acid; major industrial use is the production of phosphoric acid
Tert-Butyl hydroperoxide	Used in a variety of oxidation processes, industrially, is used as a starter of radical polymerization
Tetrahydrofuran	One of the most polar ethers; a useful solvent; its main use is as a precursor to polymers
Tetramethylsilane	The simplest tetraorganosilane; a building block in organometallic chemistry
Thionyl chloride	An inorganic compound; used in chlorination reactions; converts carboxylic acids to acyl chlorides
Thiophenol	An organosulfur compound; the simplest aromatic thiol

Titanium tetrachloride	An intermediate in the production of titanium metal and titanium dioxide
Tollens' reagent	A chemical test most commonly used to determine whether a known carbonyl-containing compound is an aldehyde or a ketone
Triphenylphosphine	Used in the synthesis of organic and organometallic compounds.

LABORATORY SAFETY

GENERAL SAFETY RULES:

1. The safe way is the right way to do your job. Plan your work. Follow instructions. If you do not know how to do the experiment safely, ask your teaching assistant.
2. Be able to use all safety devices and protective equipment provided for your use and *know their location* (eyewash fountain, shower, fire blanket, fire extinguisher).
3. Safety goggles must be worn at all times.
4. *Do not* eat or drink in the laboratory (and do not store food in the refrigerators). Smoking in the laboratory is absolutely forbidden.
5. Horseplay in any form is dangerous and prohibited. Do not run in laboratory areas.
6. Report to your TA all unsafe conditions, unsafe acts, and "near misses" that might cause future accidents. Report any accident or fire, no matter how trivial, to the TA.

Hazardous Chemicals:

- (a) Be especially mindful of fire hazards when you or your lab neighbors are working with flammable liquids.
- (b) Hazardous Substances: Know common explosive, toxic, and carcinogen materials and use them only with adequate safeguards.
- (c) Never leave a reaction or experiment running unattended, unless you have told your lab partners enough about it to deal with potential hazards while you are away.
- (d) Keep hood and bench top areas clean and workable space maximized.

Disposal of solvents, chemicals and other materials:

Never pour solvents or reactive chemicals down a drain. Such careless handling of flammable or toxic liquids presents a serious hazard in the laboratory. Also, never keep an open beaker of such solvents outside a hood. Chlorinated solvents are poured into solvent waste containers kept inside the hoods. When in doubt about how to dispose of something, ask a TA. If drain disposal is necessary and acceptable, always flush the drain before, during, and afterwards with a lot of water, always using the drains in the hoods. All glass must be discarded in the specially designed containers. A dustpan and brush for broken glass can be checked out of Lab Supplies. Spilled mercury is a special safety hazard and should be reported to your TA for cleanup.

IDENTIFICATION OF ANIONS

The inorganic qualitative analysis involves the identification of ions present in a sample. The salt consists of anion and cation. The basis of identification is the observed chemical behaviour of the components. The salt analysis may be systematically carried out in the following three steps:

- i) Preliminary examination
- ii) Detection of anions and
- iii) Detection of cations

CLASSIFICATION OF ANIONS (ACIDIC RADICALS)

The anions are provided by the acids in the process of salt formation; hence these are generally referred to as acidic radicals. These radicals cannot be divided in the systematic groups as has been done in the case of the cations. However, for the sake of simplicity, these have roughly been divided into three groups depending upon their reactions with certain reagents.

Classification of acidic radicals or anions:

Group	Name and formula of the Radical	Group Reagent	Inference of the group
Class I anions (First group)	Carbonate (CO_3^{2-}) Sulphite (SO_3^{2-}) Sulphide (S^{2-}) Acetate (CH_3COO^-) Nitrite (NO_2^-) Thiosulphate ($\text{S}_2\text{O}_3^{2-}$)	Dil. HCl or H_2SO_4 (Cold or hot.)	Gases of different colours and smells are evolved.
Class II anions (Second group)	Chloride (Cl^-) Bromide (Br^-) Iodide (I^-) Nitrate (NO_3^-) * Oxalate ($\text{C}_2\text{O}_4^{2-}$) * Borate (BO_3^{3-}) * Fluoride (F^-)	Conc. H_2SO_4 (hot.)	Gases of different colours and smells are evolved.

Class III anions (Third group)	Sulphate (SO_4^{2-}) * Phosphate (PO_4^{3-})	Barium chloride (BaCl_2) in presence of dill. HCl. Ammonium molybdate ($\text{NH}_4)_2\text{MoO}_4$ in presence of conc.	A white precipitate appears. A yellow precipitate appears.
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		HNO ₃ .	
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* Interfering radicals (or anions)

PRELIMINARY TEST FOR THE ANIONS

A preliminary test for the anions is done on the basis of their class or group.

Preliminary Tests for the Anions of Class I (Group I)

The salts of these anions are decomposed by dil. H₂SO₄ or dil. HCl which serves as their group reagent. These anions with their preliminary tests are summarized below.

Take a small amount of salt or mixture in a dry test tube and add 5-6 ml of dil. H₂SO₄ or dil. HCl. Observe the reaction taking place in the test tube. If there is no reaction, heat the contents of the test tube gently and observe the sound, colour and odour of the gas evolved. From the observation, guess the presence of the anion according to the following table:

S. No.	Anion	Experiment	Observation	Inference
1.	Carbonate anion (CO ₃ ²⁻)	On conducting the above experiment with dil. acids in cold or on heating.	*Brisk effervescence with evolution of colourless, odourless gases (CO ₂).	CO ₃ ²⁻ may be present.
2.	Sulphite anion (SO ₃ ²⁻)	In the above experiment.	If the colorless gas with suffocating odour of burning sulphur is evolved (SO ₂)	(SO ₃ ²⁻) may be present.
3.	Sulphide anion (S ²⁻)	On conducting the above experiment.	** Evolution of colourless gas with smell of rotten eggs occurs (H ₂ S)	(S ²⁻) may be present.
4.	Nitrite anion (NO ₂ ⁻)	In the above experiment.	***Brown fumes with pungent odour (NO ₂) are evolved.	NO ₂ ⁻ may be present.
5.	Thiosulphate anion (S ₂ O ₃ ²⁻)	On conducting the above experiment.	If the colorless gas with suffocating odour	(S ₂ O ₃ ²⁻) is expected to be

			is evolved and solution in test tube becomes yellowish white with turbidity.	present.
6.	Acetate anion (CH ₃ COO ⁻)	The same experiment as has been given above is conducted and thus	Small of vinegar is noticed without evolution of any gas (CH ₃ COOH)	(CH ₃ COO ⁻) is expected to be present.

Note:

* Basic carbonates of Pb and Bi do not evolve CO₂ with effervescence, but do so gradually.

**Many sulphides, e.g. those of Ag, Hg, As, Co and Ni do not decompose on heating with dil. HCl or dil. H₂SO₄. Therefore, the salt or mixture is heated with conc. HCl alone or with little zinc to observe the evolution of H₂S. If no H₂S smell is noticed, the above sulphides are taken as absent.

***All nitrites are soluble in water. The liberated NO₂ gas turns FeSO₄ solution black.

Preliminary Tests for the Anions of class II (group II).

The group reagent for the anions of this class is conc. H₂SO₄, i.e., the salts of these anions are readily decomposed by conc. H₂SO₄. After performing the preliminary tests of the anions of group I or class I, take a small amount of the salt or mixture in a separate dry test tube and add conc. H₂SO₄(2-3ml). then heat gently for some time. Observe the reactions occurring in the test tube as well as the gases evolved according to the following table.

S. No.	Anion	Experiment	Observation	Inference
1.	Chloride anion (Cl ⁻)	In the above experiment,	Colorless pungent gas (HCl) is evolved	(Cl ⁻) may be present.
2.	Bromide anion (Br ⁻)	In the above experiment,	Red brown gas (Br ₂) is evolved and solution becomes orange.	Br ⁻ is expected.
3.	Iodide anion (I ⁻)	On conducting the above reaction.	Dark violet fumes (I ₂) are observed	(I ⁻) May be present.
4.	Nitrate anion	In the above	* Pungent light	(NO ₃ ⁻)

	(NO ₃ ⁻)	reaction.	brown gas (NO ₂) is evolved.	may be present.
5.	Oxalate anion (C ₂ O ₄ ²⁻)	On conducting the above experiment (strong heating),	**colorless, odourless gas is evolved which burns with blue flame at the mouth of the test tube on bringing a burning stick near the mouth	(C ₂ O ₄ ²⁻) is expected
6.	Fluoride anion (F ⁻)	On strong heating the contents of the test tube.	White pungent smelling gas is evolved and test tube becomes greasy	(F ⁻) is expected
7.	Borate anion (BO ₃ ³⁻)	The borates are not decomposed by only conc. H ₂ SO ₄ but in presence of ethyl alcohol or CaCl ₂ , they give compounds which can easily be detected. It will be discussed latter.		

Note: * All nitrates are soluble in water.

**Oxalates of K⁺ and NH₄⁺ are soluble in water. Ferrous oxalate is sparingly soluble. All other oxalates are insoluble.

PREPARATION OF SOLUTION FOR IDENTIFICATION OF THE ANIONS

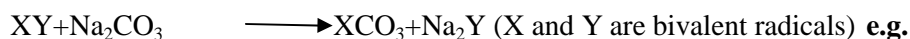
For the identification of the anion(s) in the salt or the mixture, the anion (s) must be brought in solution, i.e., in free state so that the anion (s) may give suitable tests with the suitable reagent (s). Many salts are soluble in water to give free anions and cations in solution, e.g. most of the ammonium salts and those of alkali metals are soluble. All nitrites, nitrates, acetates and many halides are also soluble in water. In the aqueous solution many anions can be detected. It is usually better to bring the anion (s) into the solution as soluble sodium salts by preparing soda or sodium carbonate extract which is obtained after boiling the salt or mixture with an excess of sodium carbonate solution.

Preparation of Soda Extract:

Mix one part of the solid salt or mixture with 3 parts by weight of sodium carbonate and 10-12 ml. distilled water (mineral free) and boil for about 8-10 minutes in a beaker or conical flask. Filter the contents while hot. The filtrate, known as soda extract, is used for detecting (or testing) most of the anions. The residue left on the filter paper may be dissolved in water or dil. HCl and tested for basic radicals whose salts are insoluble both in dil. and conc. HCl.

The excess sodium carbonate taken reacts with salts or mixture of the salts whereby the anions or acidic radicals are converted to their corresponding sodium salts which are water soluble and can be filtered off. Thus the anions come down in the filtrate along with the excess of sodium carbonate. The cations or the basic radicals are converted into their corresponding carbonates almost all of which are insoluble in water and therefore remain as residue on the filter paper along with unchanged salts (amm. carbonate is soluble).

Let X represents the basic radical (cation) and Y the acidic radical (anion) of any salt. When such a salt (XY) is heated with excess of sodium carbonate, the following reactions take place:



The filtrate so obtained after neutralization with suitable acid, can be used to detect certain anions. The acid is to be added in excess till bubbles cease to evolve. This indicates the complete neutralization of the solution (soda extract). The common anions which can be identified easily using soda extract along with the acid used for its neutralization and the reagent added for the identification are given in the following table:

Anion	Experiment	observation	Inference
Cl ⁻ , Br ⁻ , I ⁻	dil. HNO ₃	AgNO ₃ soln.	AgCl: white ppt, AgBr: light yellow ppt., AgI: yellow ppt.
NO ₃ ⁻	dil. H ₂ SO ₄	Freshly prepared FeSO ₄ solution	Brown ring of FeSO ₄ . NO compd. results.
SO ₄ ²⁻	dil. HCl	BaCl ₂ soln.	BaSO ₄ : White ppt.
C ₂ O ₄ ²⁻	dil. CH ₃ COOH	CaCl ₂ soln.	CaC ₂ O ₄ : White ppt.
CH ₃ COO ⁻	dil. HCl	Neutral FeCl ₃ solution.	Basic ferric acetate: brownish red ppt.
PO ₄ ³⁻	dil. HNO ₃	Conc. HNO ₃ + (NH ₄) ₂ MoO ₄ , heated and cooled.	Canary yellow ppt.

Here,

Column 1 represents the acidic radicals whose sodium salts are found in the extract.

Column 2 gives the acid to be added for neutralizing the excess of sodium carbonate.

Column 3 contains the names of the reagents added for the identification.

Column 4 represents the characteristic changes which are observed during identification of the said anions.

Following are the advantages of preparing soda extract:

- (i) It removes the basic radicals which may interfere in the systematic identification of the anions, by converting them into insoluble metal carbonates.
- (ii) The identification of anions becomes easier in the case of compounds insoluble in water and dil. acids.
- (iii) It helps in the identification of certain basic radicals (cations) of compounds insoluble in water, conc. HCl, HNO₃, etc. For example: BaSO₄, SrSO₄, etc.

Precaution: Na₂CO₃ used in the preparation of soda extract should be pure, free from chloride and sulphate which are generally present as impurities.

Note: Carbonate ion (CO₃²⁻) is not detected by this method because it already comes from sodium carbonate. Hence it should be detected in the solid salt or mixture.

CONFIRMATORY TESTS FOR THE ANIONS

The presence of the anions in the salt or mixture is confirmed after the preliminary tests have been done. The confirmatory test for various anions is carried out as follows:

1. CO₃²⁻ anion:

If the colourless gas evolved during the preliminary test is passed into lime water*, it turns milky due to the formation of calcium carbonate, CaCO₃. If passing CO₂ is continued for a long time (excess), milky colour disappears, i.e., becomes soluble due to the formation of calcium bicarbonate, Ca(HCO₃)₂. This confirms the presence of CO₃²⁻ ion.

Note. SO₃²⁻ ion also gives the same test Hence the presence CO₃²⁻ ion is confirmed after

testing for SO₃²⁻ ion. It is better to test both CO₃²⁻ and SO₃²⁻ ions simultaneously.

2. SO₃²⁻ anion:

(i) If the colorless gas evolved during the preliminary test is brought in contact with the filter paper moistened with acidified potassium dichromate, solution**, the paper turns green.

(ii) Take 1ml. soda extract, add to it acetic acid in excess to make it neutral. Then add to it BaCl₂ solution and filter. To the filtrate, add bromine water and heat, white precipitate of BaSO₄ is obtained. These tests confirm the presence of SO₃²⁻ ion.

3. S²⁻ anion:

(i) If the colorless gas evolved during the preliminary test turns filter paper dipped in lead acetate solution black on bringing it at the mouth of test tube, it confirms the presence of S²⁻ ion.

(ii) Take 1 ml. soda extract and add to it few drops of sodium nitroprusside, the solution becomes violet, again confirming the presence of S²⁻ ion.

4. NO₂⁻ anion:

(i) If the brown gas evolved during the preliminary test turns paper dipped in starch + KI solution blue, presence of NO₂⁻ ion is confirmed.

- (ii) Add 2-3 drops of KI and starch solution in the test tube during the preliminary test, deep blue or violet color if appears, it again confirms the presence of NO_2^- ion.

5. $\text{S}_2\text{O}_3^{2-}$ anion:

- (i) If SO_3^{2-} , S^{2-} or SO_4^{2-} is present, shake a portion of the soda extract with CdCO_3 or PbCO_3 and then with $\text{Sr}(\text{NO}_3)_2$ solution. Filter and discard the precipitate if formed. Use filtrate for the detection of thio sulphate ion. If S^{2-} , SO_3^{2-} , or SO_4^{2-} is absent, use the water extract for testing $\text{S}_2\text{O}_3^{2-}$. The mixture solution + $\text{AgNO}_3 \rightarrow$ white precipitate. This ppt. is unstable and decomposes on warming or on addition of HCl into black Ag_2S through colour change from yellow to brown and finally black.
- (ii) Soda extract of the substance + iodine solution \rightarrow decolorization of iodine solution confirms the presence of $\text{S}_2\text{O}_3^{2-}$ anion.

6. CH_3COO^- anion:

- (i) A water extract of the substance gives blood-red colour in cold with neutral ferric chloride, solution, confirming the presence of acetate ion.
- (ii) On rubbing the substance + oxalic acid (few crystals) + water (few drops) between the fingers, smell of vinegar is noticed again confirming the presence of acetate ion.
- (iii) Solution of the substance + a little ethyl alcohol + a little conc. H_2SO_4 + heat gently \rightarrow fruity smell is noticed (of ethyl acetate).

Note. *Method of passing CO_2 gas into water: If the delivery tube is available, insert its two ends with corks in the sample tube and line water tube (Delivery tube must be dipped in lime water) and heat the contents of sample (mix.+acid) tube. Otherwise collect the evolved CO_2 in a test tube which just fits in the mouth of sample tube. After heating the sample tube, close the mouth of the second test tube with the thumb and add lime water to it to check the presence or thumb and add lime water to it to check the presence or absence of CO_2 gas.

**Preparation of acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution: Take approx. 1gm. of $\text{K}_2\text{Cr}_2\text{O}_7$ crystals and dissolve in 5ml. water, then add 2-3ml. dil. H_2SO_4 . This is acidified dichromate solution.

***The shelf FeCl_3 contains free HCl in small amount due to hydrolysis of FeCl_3 . Add a very dilute solution of NH_4OH drop wise to a little FeCl_3 solution taken in a test tube and shaking after each addition till a permanent precipitate is formed. Now boil the contents of the test tube and filter. The filtrate is known as neutral ferric chloride.

7. Cl^- anion:

- (i) On bringing a glass rod dipped in NH_4OH near the mouth of the test-tube during the preliminary test, white dense fumes of NH_4Cl are formed.
- (ii) On heating the given mixture with conc. H_2SO_4 and MnO_2 , greenish yellow, pungent smelling gas (Cl_2) is evolved.
- (iii) Soda extract + dil. HNO_3 + AgNO_3 solution \rightarrow a white precipitate (AgCl) is formed which is soluble in NH_4OH solution.

- (iv) Chromyl chloride test: Heat a small amount of the mixture, add to it solid $K_2Cr_2O_7$ (3 times of mixture) and conc. H_2SO_4 . Orange-yellow vapours of chromyl chloride (CrO_2Cl_2) are evolved and are collected in a test-tube containing NaOH. This is acidified with CH_3COOH and treated with lead acetate solution. A yellow precipitate of lead chromate ($PbCrO_4$) is formed.

All these tests confirm the presence of Cl^- ion.

Note. The chromyl chloride test does not respond in case of chlorides of Ag, Hg, Pb and Sn. In such cases, it can be performed by the residue obtained on evaporating 5 ml. of soda extract.

8. Br^- anion:

- (i) On heating the given salt or mixture with a little MnO_2 and conc. H_2SO_4 , red-brown vapours of Br_2 are evolved.
- (ii) Soda extract+dil. HNO_3+AgNO_3 solution→ a pale yellow precipitate is formed ($AgBr$) which is partially soluble in NH_4OH .
- (iii) Soda extract+ a little dil. HNO_3 (to neutralise)+ few drops of chloroform or CCl_4+Cl_2 water or conc. HNO_3 + Shake →chloroform or CCl_4 layer (lower) becomes yellow or orange. These tests confirm the presence of Br^- ion.

9. I^- anion:

- (i) Given salt or mixture+ $MnO_2+conc. H_2SO_4+heat$ →violet vapours (I_2) in excess are evolved which turn the paper dipped in starch solution blue.
- (ii) Soda extract+dil. HNO_3+AgNO_3 solution→yellow precipitate of AgI is formed which is insoluble in NH_4OH solution.
- (iii) Soda extract+ a little $HNO_3(dil.)$ (to neutralize)+ few drops of $CHCl_3$ or $CCl_4+conc. HNO_3$ or Cl_2 water+ shake well→layer of organic liquid becomes pink or violet. These tests confirm the presence of I^- ion.

10. NO_3^- anion:

- (i) On heating the salt or mixture with copper turnings and conc. H_2SO_4 , deep brown fumes (NO_2) are evolved in excess but the solution does not become yellow or pink.
- (ii) Aqueous extract or solution of the salt or mixture in dil. HCl + freshly prepared solution of $FeSO_4+shake well+add gradually conc. H_2SO_4$ by the side of the test tube→a brown ring of $FeSO_4$. NO is formed at the junction of two liquids (This is called ring test)

The above tests confirm the presence of NO_3^- ion.

11. $C_2O_4^{2-}$ anion:

- (i) Take soda extract of the salt or mixture in a test tube, acidify it with excess of CH_3COOH and then add $CaCl_2$ solution. A white precipitate of CaC_2O_4 is formed. Dissolve the precipitate in dil. H_2SO_4 and warm it. To the warm

solution, add few drops of KMnO_4 solution and shake, pink colour of KMnO_4 solution disappears.

- (ii) Take a little salt or mixture in a test-tube, add dil. H_2SO_4 and heat till effervescence ceases to appear. Add a pinch of MnO_2 and heat again. Effervescence due to evolving CO_2 reappears.

The above tests confirm the presence of $\text{C}_2\text{O}_4^{2-}$ ion.

12. F^- anion:

- (i) Take a little salt or mixture with some sand in a test tube, add conc. H_2SO_4 to it and heat, bring a glass rod moistened with water at the mouth of the test tube. A waxy white deposit on the glass rod is obtained (NH_4Cl and HgCl_2 also leave a white deposit on the rod but this deposit is crystalline and not waxy).

After performing this test the contents of the test tube should not be thrown in the sink without cooling and diluting.

- (ii) Soda extract + CH_3COOH (to neutralise) + CaCl_2 solution + shake \rightarrow white precipitate appears after sometime. To the precipitate add dil. H_2SO_4 + heat + KMnO_4 solution \rightarrow pink color of KMnO_4 is not discharged.

These tests confirm the presence of F^- ion.

13. BO_3^{3-} anion:

- (i) Take a little salt or mixture in a porcelain dish, add a little conc. H_2SO_4 just to make the paste of the substance, 1/2ml. of ethyl alcohol or methylated spirit well by a glass rod and ignite \rightarrow a green edged flame is developed (copper and barium salts also give the same test and interfere in the detection of BO_3^{3-} ion by this test. Hence test should be performed in a test tube instead of porcelain dish and the vapours evolved after heating should be burnt at the mouth of the test-tube).

- (ii) Make a paste of little mixture + calcium fluoride (CaF_2) with a little conc. H_2SO_4 . Take a portion of this paste with a thin glass rod or Pt-wire and bring it near the edge of the flame (do not introduce the paste into the flame) \rightarrow green flame is obtained (Cu & Ba-salts do not interfere).

These tests confirm the presence of BO_3^{3-} ion.

14. SO_4^{2-} anion:

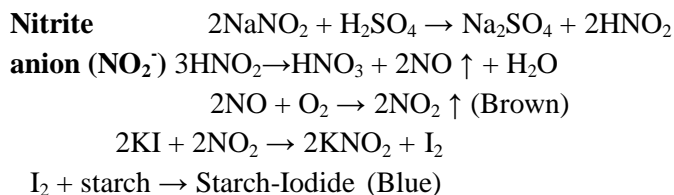
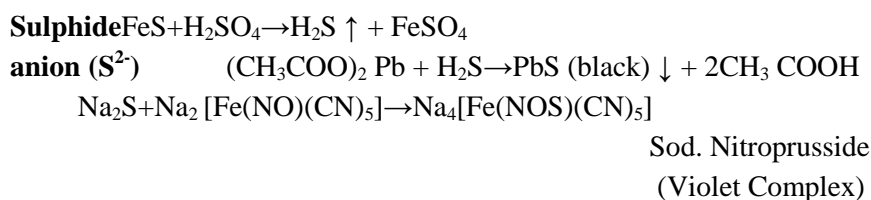
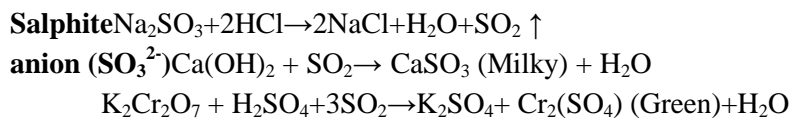
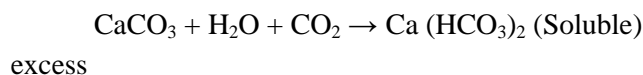
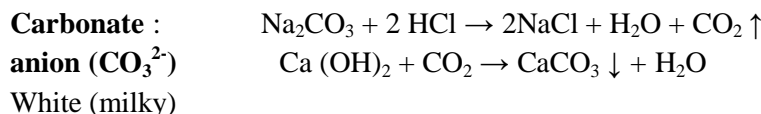
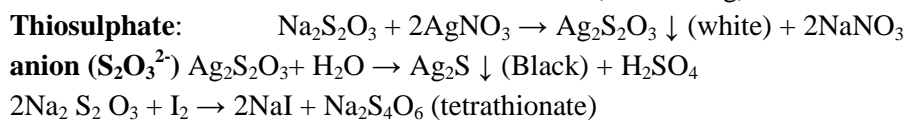
Take the solution of the substance in dil. HNO_3 or soda extract + dil. HCl . Add BaCl_2 solution. A curdy white precipitate is formed (BaSO_4) which is insoluble in all the conc. acids. This confirms the presence of SO_4^{2-} ion.

15. PO_4^{3-} anion:

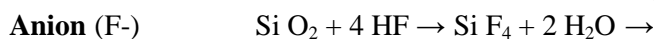
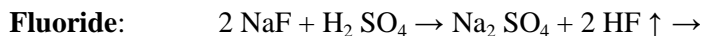
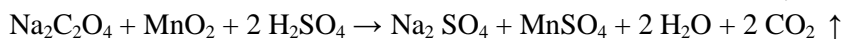
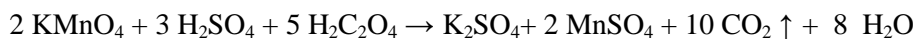
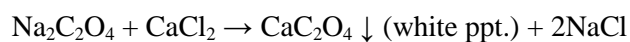
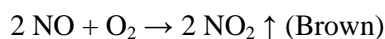
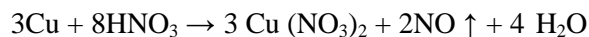
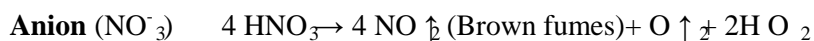
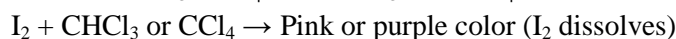
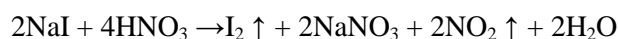
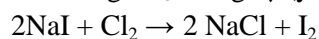
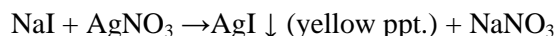
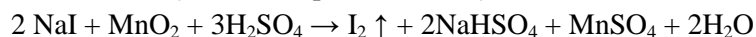
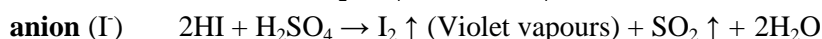
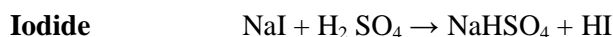
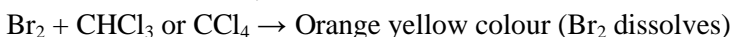
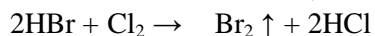
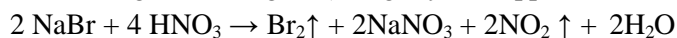
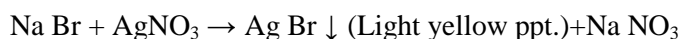
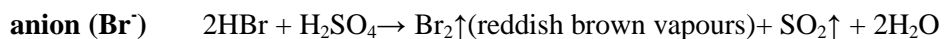
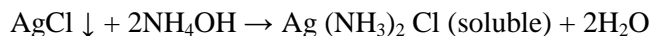
- (i) Boil a little substance with conc. HNO_3 and add ammonium molybdate solution to it, boil again and cool. A canary yellow precipitate is formed which is soluble in ammonium and alkali hydroxides.

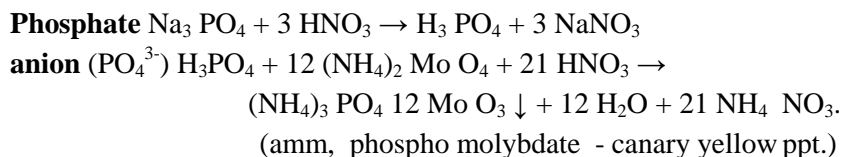
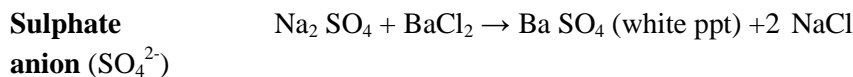
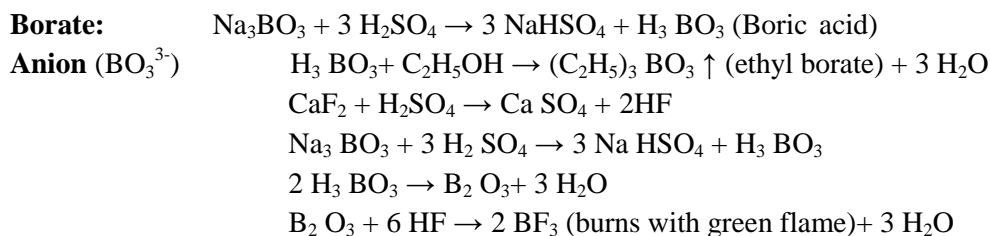
- (ii) This ion can also be tested in the soda extract as has already been given above. These are the confirmatory tests for PO_4^{3-} ion.

- (iii)

Reactions Involved:**Ring test:****Acetate:****Anion (CH_3COO^-)****Chloride anion (Cl^-)**

(greenish yellow gas)





Special Tests for the Mixtures of Anions (Combinations).

1. Carbonate and Oxalate.

If given as a combination in a mixture, decompose carbonate anion completely by dil. H_2SO_4 (oxalate remains unaffected and then add MnO_2 . If effervescence appears again, it indicates the presence of oxalate which can be confirmed by decolorization of KMnO_4 solution.

2. Carbonate and Sulphite.

Carbonates and sulphites both are decomposed by dil. H_2SO_4 to give CO_2 , and SO_2 gases which give white ppt. with lime water. But sulphite only (SO_2) reacts with pot. dichromate in presence of dil. H_2SO_4 to change the colour from light yellow to green [$\text{Cr}_2(\text{SO}_4)_3$].

3. Sulphide, Sulphite and Sulphate.

Sulphide can be tested with sod. nitroprusside solution. Where, sulphite and sulphate do not interfere. If all the three anions are given together, remove sulphide by PbCO_3 or CdCO_3 as PbS (black) or CdS (yellow). Filter and add dil. HCl and BaCl_2 solution to the filtrate to give white ppt. of BaSO_4 , filter again and boil the filtrate with conc. HNO_3 or bromine water to oxidize sulphite to sulphate [$\text{Na}_2\text{SO}_3 + \text{O}$ (from HNO_3 or Br_2 water) which can be tested with BaCl_2 solution (white ppt. BaSO_4 appears again).

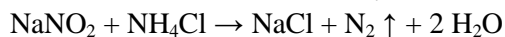
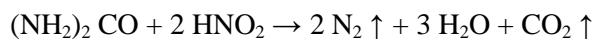
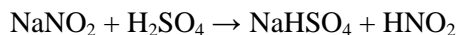
4. Chloride, Bromide and Iodide.

Chloride is tested by chromyl chloride test where bromide and iodide do not interfere. Bromide and iodide given together are tested by organic layer test. Acidify one ml. soda extract with dil. HCl or dil. H_2SO_4 , add few drops of CHCl_3 or CCl_4 followed by freshly prepared chlorine water drop by drop while shaking. If organic layer is pink or violet, iodide is confirmed. Continue adding excess of

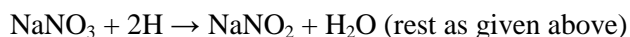
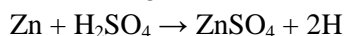
chlorine water with vigorous shaking. If organic layer becomes orange brown or yellow, bromide is also confirmed.

5. Nitrite and Nitrate.

If nitrite gives positive test as given above, decompose it by urea or NH_4Cl as below:



Now reduce nitrate using zinc and dil. H_2SO_4 to nitrite and test it by KI and starch solution as given below:



6. Nitrite and Iodide.

If both are preset in the mixture, add conc. H_2SO_4 to it heat and then add starch solution. Blue color of starch iodide confirms the presence of both anions.

7. Nitrate and Bromide.

Reduce nitrate to nitrite by zinc and dil. H_2SO_4 and test as usual.

Confirm bromide by organic layer as usual.

8. Nitrate and Iodide.

Reduce nitrate to nitrite and then nitrite and iodide can be tested by starch solution (blue). Iodide can also be detected by organic layer test.

The reactions of the tests for combination of acidic radicals or mixtures of anions are the same as given above. Therefore the reactions involved in the tests can be referred to the above.

IDENTIFICATION OF CATION (KNOWN)

The separation of Cations in to analytical Groups: The precipitation of Group I cations, the separation of Group II cation from Group IV Cations, The Precipitation of Group III Cations, The Precipitation of Group V Cations.

Preliminary Investigation of the Sample

Preparation of solution for the analysis of Cations

Separation of cation into Analytical Groups

Analysis of the cations of Analytical Group I: Separation and Identification of the cations of Analytical Group I

Analysis of the cations of analytical Group II: Separation of Analytical Group II in to group IIA and Group IIB, Separation of the Cations of group IIA, Separation of the Cations of group IIB, Identification of the cations of Group II

Analysis of the cations of analytical Group III: Separation and Identification of the cations of analytical Group III.

Analysis of the cations of analytical Group IV: Separation and identification of the cations of Analytical group IV.

Analysis of the cations of analytical Group V: Separation and identification of the cations of Analytical group V.

Analysis of the Cations of analytical group VI

Chemical reactions involved in the test of basic radicals

CLASSIFICATION OF CATIONS INTO ANALYTICAL GROUPS

The cations (or the basic radicals) have been classified into seven groups, viz. from zero, I to VI group according to their nature to form the precipitate with various reagents. Because no single reagent is available which could form precipitate with all the cations, hence they have been classified into groups and the cations of each group give precipitate with a particular reagent called group reagent.

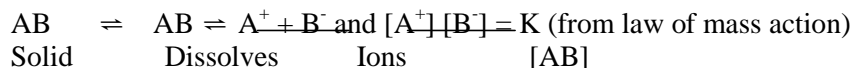
SOLUBILITY AND SOLUBILITY PRODUCT

In the simple terms if a substance dissolves in a solvent, it is said to be soluble (more accurately solute) and the resulting mixture is known as solution (may be unsaturated or saturated). This tendency of a solute to get dissolved in a solvent is called, in a general sense, its solubility. The solubility depends on the nature of both the solute (substance) and the solvent. It is more accurately defined as **“the number of grams of the substance which is dissolved in 100 grams of the solvent in a saturated solution at a given temperature.”**

The solubility of a solid substance in a given solvent depends mainly on the temperature and very slightly on the pressure. For most solid substances, it increases with increasing temperature, e.g., solubility of AgNO_3 increases rapidly but that of NaCl increases slowly. The change in solubility with changing temperature is usually expressed by means of solubility curves (plots of the number of grams of solute dissolved in 100 grams of solvent along ordinate against the temperature along abscissa) There are also some substances whose solubility decreases with rising temperature, e.g. Li_2CO_3 , NaOH , etc.

Solubility Product and Precipitation.

When a sparingly soluble substance, say AB , is kept in contact with water for sometime at a definite temperature, the following equilibrium is established:



The concentration of the unionised [AB] is constant at a given temperature if excess of AB is present. Hence, $[A^+][B^-] = K[AB] = \text{constant}$. Therefore, “**In equilibrium, the product of the ionic concentration is constant at a given temperature. This constant product, $[A^+][B^-]$, is called the solubility product (K_s)**”. When the ionic product exceeds the solubility product, the solution is super saturated and precipitation occurs but if the ionic product is less than the solubility product, the solution is unsaturated and precipitation does not occur. This is called theory of precipitation. This can also be represented as
 Ionic product < solubility product, K_s , the salt dissolves.

Ionic product > solubility product, K_s precipitation takes place.

Relation between Solubility and Solubility Product.

The solubility of a sparingly soluble substance (electrolyte) of 1:1 can be calculated using the principle of the solubility product. Let it be AB.

$$K_s(AB) = [A^+][B^-]$$

$$\text{If } [A^+] = [B^-] = s \text{ moles per liter}$$

$$K_s(AB) = s \cdot s = s^2$$

$$\text{Or } s = \sqrt{K_s}$$

Where s = solubility of AB in moles per liter and $K_s(AB)$ is the solubility product of AB.

But for the substances (electrolytes) of 1:2 or 2:1 type, i.e., AB_2 or A_2B type

$$K_s = s \times (2s)^2 \text{ or } (2s)^2 \times s = 4s^3$$

$$\therefore s = \sqrt[3]{\frac{K_s}{4}} \text{ moles per liter}$$

THE COMMON ION EFFECT

The phenomenon of lowering the degree of ionisation of a weak electrolyte substance by adding to its solution a solution of strong electrolyte having a common ion and thus decreasing the concentration of the ion other than the common ion of the weak electrolyte is known as **Common ion effect**. For example, NH_4OH , a weak base (electrolyte) dissociates in solution as $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

On applying the law of mass action $[NH_4^+][OH^-] = K[NH_4OH] = \text{constant}$, on adding strong electrolyte, NH_4Cl , $NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$, NH_4^+ ions are added to the solution. Thus the concentration of NH_4^+ ions coming both from NH_4Cl and NH_4OH (common ion)

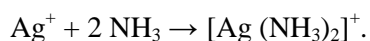
increases but K remains constant at any given temperature. As a result, the value of $[\text{NH}_4\text{OH}]$ must increase thereby decreasing the value of $[\text{OH}^-]$. This indicates that the degree of ionisation of NH_4OH is decreased by the addition of NH_4Cl which furnishes the common ion, NH_4^+ . Similarly the ionisation of H_2S , a weak electrolyte, is diminished in the presence of HCl , a strong electrolyte, giving common H^+ ions.

The principle of common ion effect is of immense importance in qualitative analysis because this provides a valuable method for controlling the concentration of the ions furnished by a weak electrolyte. The common examples are: precipitation of second group radicals as sulphides using H_2S in presence of HCl and that of fourth group cations as sulphides in presence of NH_4OH . Similarly precipitation of third group cations as hydroxides using NH_4OH in presence of NH_4Cl . The detailed account will be given in the respective groups.

Complex Formation.

Complex ion formation is of great importance in qualitative analysis (i) to dissolve a precipitate alone or from a mixture of two or more (ii) to check the precipitation of a particular cation by complex ion formation. For example,

(a) AgCl is soluble in ammonia solution due to the formation of the complex ion, $[\text{Ag}(\text{NH}_3)_2]^+$.



This capacity of Ag^+ ion is utilized in its separation from Pb^{2+} and Hg_2^{2+} ion.

(b) Separation of Cu^{2+} and Cd^{2+} ions is also based on the complex formation tendency with CN^- ions from KCN solution: $\text{K}_3[\text{Cu}(\text{CN})_4]$ and $\text{K}_2[\text{Cd}(\text{CN})_4]$. Of the two complex ions $[\text{Cu}(\text{CN})_4]^{3-}$ and $[\text{Cd}(\text{CN})_4]^{2-}$, the value of instability constant for copper complex ion is less than cadmium complex ion and hence more Cd^{2+} ions are available in the solution than Cu^{2+} ions. In presence of H_2S gas, CdS (yellow ppt) is formed but copper ion remains unaffected.



SEPARATION OF CATIONS INTO GROUPS

(i) **Precipitation of group I cations.** The cations of group I are precipitated as insoluble chlorides in the presence of dil. HCl .

(ii) Separation of group II cations from group IV cations. The cations of both these groups are precipitated as sulphides but in different media, group II cations are precipitated in acidic medium (HCl) and those of group IV in basic medium (NH₄OH). As has already been stated, the precipitation of sulphides can occur only when $[M^{2+}] [S^{2-}]$ exceeds the solubility product of the sulphide, MS at given temperature,

$$\text{i.e. } [M^{2+}] [S^{2-}] > K_S$$

In presence of HCl, due to common H⁺ ions, the ionisation of H₂S is suppressed thereby giving less concentration of S²⁻ ions in solution. Under this condition, the ionic product of metal and sulphide ions only exceeds the solubility product of sulphides of group II cations (such metal sulphides have low values of solubility products) and as a result these sulphides are precipitated. The solubility product values for sulphides of group IV cations being high are not surpassed by ionic product and these cations remain in the filtrate. These cations are then precipitated as sulphides in presence of excess S²⁻ ions in basic medium, i.e., NH₄OH.

(iii) Precipitation of group III cations. The group III cations are precipitated as hydroxides with the help of NH₄OH in the presence of NH₄Cl. NH₄Cl suppresses the ionisation of NH₄OH thereby giving less OH⁻ ions in solution, just sufficient to precipitate the group III cations and keeping higher group, i.e. IV, V & VI, cations in solution. This happens because of the low values of solubility products of the hydroxides of group III cations which are surpassed by ionic products of [OH⁻] and [M³⁺].

(iv) Precipitation of group V cations. These cations are precipitated as carbonates using (NH₄)₂CO₃ in presence of NH₄OH when Mg remains in solution.

PRELIMINARY INVESTIGATION OF THE SAMPLE

Basic radicals or cations in a sample can be tested by two types of tests:

(1) Dry tests, (2) Wet tests.

(1) Dry tests: These are the preliminary tests and include the following:

(a) Dry heating test

(b) Flame test

(c) Borax bead test

(d) Cobalt nitrate test

(e) Charcoal cavity test

(f) Microcosmic bead test

Of these, flame test, borax bead test, cobalt nitrate test and charcoal cavity test are more important and impart more valuable information about the cations in the sample under investigation.

(b) Flame test. Chlorides of certain metals when heated strongly using a loop of Pt-wire cleaned by conc. HCl, are volatilized easily in non-luminous flames of bunsen burner and their vapours become incandescent in the flame. The salt or group ppt. is picked by Pt-wire loop and kept into the edge of non-luminous flame. The imparted colour by the metals can be observed by naked eye:

Na – golden yellow, K-violet, Cu-bluish green,

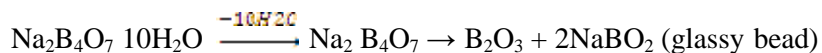
Ca – brick or dull red, Sr – crimson red, Ba- apple green.

(C) Borax bead test. This test is performed mainly for the coloured substances and sometimes for white substances leaving coloured residue on dry heating.

The loop at the tip of the Pt-wire is heated in the flame, then dipped into borax powder, heated again strongly till borax swells up and finally converted into a transparent glassy bead. This bead is touched with the substance or group ppt. heated strongly in non-luminous flame and then in luminous flame, and color is observed.

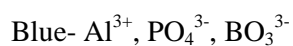
Cation	Non-luminous flame (Oxidising)	Luminous flame (reducing)
Copper	green or light blue	red or colorless
Iron	Yellow	bottle green
Chromium	Green	Green
Cobalt	deep blue	deep blue
Nickel	light brown	Black
Manganese	Violet	Colorless

Chemistry of borax bead test: On strongly heating borax transforms into glassy bead:



B_2O_3 combines with basic oxides to form meta borates which have characteristic colours.

(d) Cobalt nitrate test. Cobalt nitrate on heating is decomposed to CoO which combines with certain metallic and non-metallic oxides to give colored compounds. The powdered substance or mixture is mixed with an equal amount of solid Na_2CO_3 placed in a charcoal cavity, moistened with water and heated with the help of blow pipe. It is then moistened with few drops of cobalt nitrate and heated again. The color of the residue indicates the radical.



Green- Zn^{2+}

Dirty blue-green- Sn^{2+}

Pink- Mg^{2+}

Example. $Zn SO_4 Na_2CO_3 \rightarrow Zn CO_3 + Na_2 SO_4$

$ZnCO_3 \rightarrow ZnO + CO_2 \uparrow$

$2CO (NO_3)_2 \rightarrow 2Co O + 4 NO_2 \uparrow + O_2 \uparrow$

$Zn O + Co O \rightarrow Zn O. Co O \rightleftharpoons Co Zn O_2$

(e) Charcoal cavity test. In this test, the powdered sample is mixed with an equal amount of solid Na_2CO_3 , placed in a charcoal cavity, moistened with water and strongly heated in a reducing flame by means of blow pipe. From the color of the bead or deposit round the cavity (incrustation), cation/metal is identified.

Hot residue Cold residue Inference

Yellow White Zn

Reddish brown reddish brown Cd

Brown yellow Pb

Orange yellow Bi

Yellow white Sn

White white As, Al, Mg, Ca, Ba

Red Red Cu

Black white Fe, Co, Ni, Mn

(2) **Wet tests.** These are most important tests and are performed to confirm the presence of almost all the cations. The first step for the wet tests is the preparation of the original solution.

METHODS FOR THE PREPARATION OF ORIGINAL SOLUTION

The solution that contains all the cations is known as original solution. It can be prepared as follows:

- (i) A little of the mixture sample is boiled with water with shaking. If does not dissolve then,
- (ii) Mixture is boiled with dil. HCl. Still if does not dissolve then,
- (iii) About 1gm mixture is boiled with 5ml. conc. HCl in 100ml beaker for a while, diluted with water and boiled again. Mostly the mixture is dissolved and solution becomes transparent.
- (iv) If the mixture is insoluble in conc. HCl, then solubility should be observed in least quantity of dil. HNO₃, then conc. HNO₃ and finally in aqua regia.
- (v) If the solution is made in HNO₃ or aqua regia, it has to be evaporated to dryness and dry residue is dissolved in dil. HCl or water after boiling. Sulphuric acid is never used as a solvent as it precipitates Ba, Sr, Ca & Pb as sulphates which are insoluble even in aqua regia.

SEPARATION OF CATIONS INTO ANALYTICAL GROUPS

On the basis of solubility product and reagents, the cations are divided into the following six groups:

1. First group: Pb²⁺, Ag⁺, Hg₂²⁺ (ous)
2. Second group A : Pb²⁺, Cu²⁺, Bi³⁺, Cd²⁺, Hg²⁺ (ic)
B : As³⁺, Sb³⁺, Sn²⁺ + (ous), Sn⁴⁺ (ic)
3. Third group: Al³⁺, Cr³⁺, Fe³⁺
4. Fourth group: Ni²⁺, Co²⁺, Zn²⁺ Mn²⁺
5. Fifth group: Ba²⁺, Sr²⁺, Ca²⁺
6. Sixth group: Mg²⁺

Zero group is also there containing NH₄⁺ ion.

The cations, group reagents and salts precipitated along with their colors are summarized below:

5. Fifth group: Ba²⁺ Sr²⁺ Ca²⁺

6. Sixth group: Mg²⁺

Zero groups are also there containing ion. NH₄²⁺

The cations, group reagents and salts precipitated along with their colors are summarized below:

S.No.	Group	Group Radiclas	Group Reagent	Salt Reprecipitated	Colour of the precipitate
1.	First Group	Ag ⁺ , Pb ⁺⁺ , Hg ₂ (ous)	Dil. HCl	(Chlorides) AgCl,	White ppt.

				AgCl, PbCl ₂ , HgCl ₂	
2.	Second group	Pb ⁺⁺ , Hg ⁺⁺ (ic.) Bi ⁺⁺⁺ , Cu ⁺⁺⁺ , Cd ⁺⁺ , Sb ⁺⁺⁺ , Sn ⁺⁺ , Sn ⁺⁺⁺ , Sn ⁺⁺⁺⁺ (ic), As ⁺⁺⁺	Dil. HCL+ <i>H₂S</i>	(Sulphides)	Black ppt. (Sometimes red ppt.)
3.	Third group	Al ³⁺ Cr Fe ²⁺	After removing <i>H₂S</i> boil the solution with <i>V₂</i>	(Hydroxides) Al(<i>OH</i> ₃) Fe(<i>OH</i> ₃) <i>Cr(OH</i> ₃)	White ppt. Brown ppt. Green ppt.
4.	Fourth group	<i>Ni⁺⁺</i> <i>Co⁺⁺, Zn⁺⁺, Mn⁺⁺</i>	Third Group	(sulphides) Zns	White or state ppt. Chocolate-pink ppt. Black ppt. White ppt.
5.	Fifth group	<i>Ba⁺⁺, Sr⁺⁺, Ca⁺⁺</i>	Boil off <i>H₂S</i> and then add <i>NH₄Cl + NH₄Oh</i>	(Carbonates) BaCO ₃ , CaCO ₃ , SrCO ₃	Black ppt. White ppt.
6.	Sixth Group	<i>Mg⁺⁺</i>	& () <i>Na₂CO₃</i> and shake well. Fifth Group (Phosphate)) Filtrate+ <i>Na₂HPO₄</i> Solution	(Phosphate) <i>MgNH₄PO₄</i>	White crystalline ppt.

Important Hints for proceeding with the tests of Basic Radicals

- (i) Group reagents should be added in systematic order.
- (ii) A little excess of the group reagent must be added to ensure the complete precipitation for the group radicals.

- (iii) Solution in every group, if after adding group reagent is heated, granular precipitate is obtained.
- (iv) The volume of the solution should not be unnecessarily increased at any step. If the volume of solution at any stage has become too large (in spite of great precautions) do not throw any a portion. Put it in a dish, and evaporate it to a small volume.
- (v) There are Na^+ , K^+ and NH_4^+ radicals also, among them Na^+ and K^+ are examined by flame test and for NH_4^+ radical, special test is performed.
- (vi) Group reagent is added to original solution one after another, till the ppt. in any group is obtained. The ppt. shows the presence of any radical in that group. The complete precipitation of the radical in that group should be judged by adding sufficient amount of the group reagent otherwise it will create a great disturbance in the usual analysis of the subsequent group radicals.
- (vii) Hydrogen sulphide is a very important gas reagent for the precipitation of Ind and IVth group radicals. It is prepared in the Kipp's apparatus by the action of dil. H_2SO_4 on ferrous sulphide. Through the kipp's apparatus continuous supply of the gas is available. See fig ahead.

ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP I

Analysis of first group (silver group)

A white ppt. is obtained after the addition of dil. HCL to the original solution. It is filtered and washed with water and then boiled with 5-10 ml water. Filter and keep the filtrate for II group.

Note: If solution is prepared in dil. HCL, 1st group is considered to be absent. It is not necessary that there should be complete precipitation of metallic ions of a particular group by means of that group reagent before proceeding of the next group. Mercurous salts are partially oxidized to mercuric salts and so are precipitate as mercuric sulphide also.

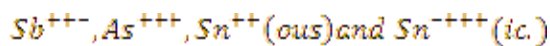
Analysis of second group

This group is divided in two groups:

- (i) IInd A group (copper Group)
- (ii) IInd B group (arsenic group)

II A copper Group:

Copper Group consists of Pb^{++} , Hg^{++} (ic), Bi^{+++} , Cu^{++} and Cd^{++} while Arsenic group contain

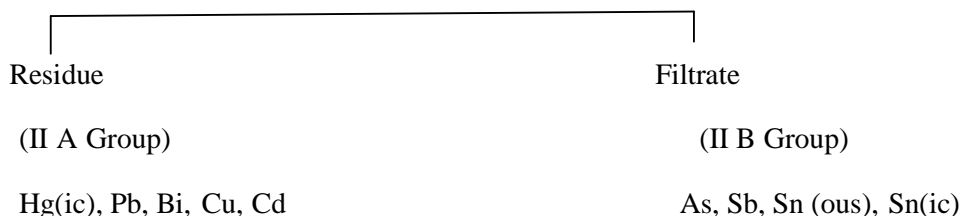


In this group H₂S is passed in a little portion of the 1st group filtrate. If precipitate does not come, then it should be diluted with water, warmed and then H₂S is passed in the rest of the solution. It is filtered and washed well with H₂S water. The filtrate is kept for III group. Different radicals give the following coloured precipitates.

Hgs	Black(sometimes red)	Cds	Yellow
Pbs	Black(or Brown)	As_2S_2	Yellow
Bi_2S_2	Brown	SnS_2	Yellow
CuS	Black(or Brown)	Sb_2S_3	Orange

Yellow ammonium sulphide contains excess of sulphur dissolved in colourless ammonium sulphide solution and is expressed as $(NH_4)_2Su$

The washed precipitate is warmed with a little yellow ammonium sulphide solution and filtered.



ANALYSIS OF THE CATIONS OF GROUP II

II A copper group- Residue is washed with water and then treated with 50% HNO_3 , boiled cooled and filtered.

Black residue It may be HgS. Dissolve it in aqua regia and evaporate it to almost dryness. Add water and divide it in two parts (i) To first part add $SnCl_2$ Soln white or	Filtrate: It may contain the nitrates of Pb, Bi, Cu. Take a little part of it add dil. H_2SO_4 . If a white ppt. appears then add alcohol and dil. H_2SO_4 to the whole filtrate and filter.		
	White residue It may contain Dissolve this residue in conc. Solution of CH_3COONH_4 and	Filtrate: It may contain Bi, Cu and Cd as nitrate. Add to it excess of NH_4OH and filter:	
	White residue: It may be	Filtrate: It may contain Cu and Cd. If it is blue Cu is there if it is colourless Cu is absent. First	

<p>grey ppt (II) To second part add Cu turnings whitish deposit on Cu Hg⁺⁺ confirmed.</p>	<p>add K₂CrO₄ yellow ppt pb (Lead) confirmed.</p>	<p>Bi(OH)₃. Dissolve the residue in the least quantity of conc. HCl divide it in two parts: (I) To first part add excess of water white ppt. (II) To second part add. Sod stannite soln. black ppt. (Bismuth confirmed)</p>	<p>Method: (i) To first part add ch₃cooh in excess K₄ Fe(CN)₆ brown coloured ppt. Cu⁺⁺ (copper) confirmed. (ii) To second part add KCN soin. Till the filtrate becomes colourless. Now pass H₂S yellow ppt. Cd⁺⁺ (cadrnium) confirmed. Second method: Add. conc. HCl and pass H₂S and filter.</p>	
			<p>Filtrate: Dilute it and pass H₂S again yellow ppt. (cadmium) confirmed.</p> <p>Black residue: Cu⁺⁺ (Copper) confirmed.</p>	
			<p>(iii) To third part add 1 c.c. of conc. HCl and FeSO₄ soln. and filter.</p>	
			<p>Residue Cu⁺⁺ (copper) confirmed.</p>	<p>Filtrate: Dilute it with water and pas H₂S gas yellow ppt. Cd⁺⁺ (Cadmium) confirmed.</p>

ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP III

IIB Arsenic Group

Dilute the filtrate with water obtained after treating the second group ppt. with yellow ammonium sulphide and dil. HCl (in excess). A coloured ppt. indicates the presence of arsenic group but if a white ppt. is obtained it shows the absence of arsenic group radicals and reject it. Fiter the ppt. and boil it with conc. HCl and filter.

<p>Yellow residue: It may be As₂S₃. Dissolve it in conc. HNO₃ and add</p>	<p>Filtrate : It may contain chlorides of Sb and Sr which may be confirmed by two different methods.</p>
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ammonium molybdate solution and heat Yellow ppt. As ⁺⁺⁺ (Arsenic) Confirmed.	First Method: Make the filtrate just alkaline by adding NH ₄ OH soln. Add 1-2 gms. solid oxalic acid boil and pass H ₂ S gas. Filter if a ppt. is obtained.	
	Orange residue: It may be Sb ₂ S ₃ : Dissolve it in least quantity of conc. HCl Dilute it with water white ppt. or turbidity. Sb ⁺⁺⁺ (Antimony) confirmed.	Filtrate: It may contain Sn. To it add NH ₄ OH to make it alkaline and pass H ₂ S gas Dirty yellow ppt. Sn ⁺⁺⁺ (Stannic) confirmed
	Second Method: To the filtrate add iron filling and heat for five minutes and filter.	
	Black residue: Sb ⁺⁺⁺ (Antimony confirmed.)	Filtrate It may contain SnCl ₂ . To it add HgCl ₂ Soln. White or gray ppt. Sn ⁺⁺ (Stannous) confirmed.

ANALYSIS OF THIRD GROUP

Boil off H₂S completely (test with lead acetate paper for this) from filtrate of the second group and concentrate it. Boil it again with 1 c.c. of conc. HNO₃ as to convert all ferrous salt (if present) to ferric salt; otherwise ferrous hydroxide will not be completely precipitated in this group and thus will interfere in IVth group giving a black precipitate of Fes. Then after cooling add NH₄CL and NH₄OH (in excess) till the solution distinctly smells of ammonia.

Filter and wash the precipitate with water and keep the filtrate for IVth group. Dissolve the ppt. in 2 c.c. of H₂O₂ or in excess of Br₂water + NaOH₂, boil* it and filter. Boiling at this stage is essential since this ensures the complete oxidation of Fe⁺⁺ to Fe⁺⁺⁺

Fe(OH)₃ – Brown ppt.

Al(OH)₃ – White ppt.

Cr(OH)₃ - Green or light bluish green ppt.

Residue : Brown ppt . it may contain Fe(OH) ₃ or MnO(OH).	Filtrate : It may contain NaAlO ₂ and NaCr ₄ . if it is yellow Na ₂ CrO ₄ will be there otherwise NaAlO ₂ may be there. Divide it in two parts.
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<p>Divide the precipitate in two parts:</p> <p>(i) ppt. +conc. $\text{HNO}_3 + \text{PbO}_2$ Boil and cool By adding a little water Light, pink, violet colour Mn^{++} (Manganese) confirmed.</p> <p>(ii) Dissolve the precipitate in dil. HNO_3 or dill. HCl and divide it in two parts: To first part add $\text{K}_4[\text{Fe}(\text{CN})_6]$ deep blue colour or ppt. (b) To second part add ammonium Sulphocyanide Blood red colour Fe^{+++}(Ferric) Confirmed.</p>	<p>(a) First part $\text{CH}_3\text{COOH} + (\text{CH}_3\text{COOH})_2$ ↓ Pb Yellow ppt.</p> <p>(b) Second part + AgNO_3 Brick red ppt. Cr^{+++} (Chromium) confirmed.</p>	<p>To the part add NH_4Cl and boil White gelatinous ppt. Al^{+++} (Aluminium) confirmed.</p>
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Notes:

- (i) H_2S should be completely removed before adding conc. HNO_3 ; otherwise it will be oxidized into H_2SO_4 ; and thus will precipitate the Vth group radicals as sulphates.
- (ii) Sometimes Mn also precipitates as MnO.OH (Brown ppt.) in this group so its test becomes necessary.
- (iii) After boiling off H_2S addition of conc. HNO_3 is essential so as to convert all ferrous salts into ferric salts.
- (iv) Addition of NH_4Cl before NH_4OH is absolutely essential otherwise the basic radicals of IVth and Vth groups will precipitate out as hydroxide in this group.
- (v) Interfering radicals should be removed before proceeding in this group.
- (vi) H_2S should be passed in hot solution. At higher temperatures sulphides precipitated are granular and easy to filter.

ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP IV

ANALYSIS OF FOURTH GROUP

Some of the characteristics of the basic radicals of this fourth group are tabulated as follows:

Form of the salt	Nickel (Ni^{++})	Cobalt (Co^{++})	Zinc (Zn^{++})	Manganese (Mn^{++})
Sulphide	Black (NiS) Green- Green	Black (CoS) Pink Pink	White or Grey (ZnS) White Colourless	Light Pink(MnS) White Colourless Light pink, pink

				violet.
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Pass H_2S continuously in the hot ammonical filtrate of II group. Formation of the precipitate shows the presence of fourth group. Filter and wash the ppt. and keep the filtrate for fifth group.

Different radicals give the following coloured precipitates:

NiS	Black	ZnS	White or grey
CoS	Black	MnS	Light pink

Notes:

- (i) H_2S must be passed in hot solution otherwise ZnS and MnS will form colloidal solution.
- (ii) H_2S should not be passed for a very long time otherwise NiS and MnS will turn into colloidal solution.

Ppt. is treated with dil. HCl and filtered:

Residue: It may contain NiS and CoS. Dissolve it in aqua-regia ($3HCl + HNO_3$) and evaporate to dryness + water and divide it in number of parts.		Filtrate: it may contain $MnCl_2$ and $ZnCl_2$. Boil off H_2S , and add excess of NaOH and filter.	
To one part and NH_4OH (in excess) + dimethyl glyoxime Scarlet red ppt. Ni^{++} (Nickel) Confirmed	(i) To one part add NH_4OH (in excess) + CH_3COOH (in excess) + KNO_2 solution. Yellow crystalline ppt. Co^{++} (Cobalt) Confirmed. (ii) To other part in a porcelain dish + $NaHCO_3$ solid (in excess) + Br_2 water. Shake for some time Apple green colour (in cold) Co^{++} (Cobalt) confirmed. Apple green colour in cold changing to black on heating Co^{++} (Cobalt) and Ni^{++} (Nickel) both confirmed.	Residue White turning brown due to oxidation. (i) Dissolve the residue in conc. HNO_3 and add PbO_2 . Boil for 2-3 minutes and dilute with water Pink or violet colour. Mn^{++} (manganese) confirmed. (ii) Residue + oxidizing fusion mixture ($KNO_3 + Na_2CO_3$). Heat strongly on a porcelain piece green mass is obtained which dissolves to give pink solution Mn^{++} (Manganese) confirmed.	Filtrate: It may contain zinc. Pass H_2S in the filtrate. A white grey ppt. Zn^{++} (Zinc) confirmed.

ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP V

After boiling off H_2S , concentrate the fourth group titrate to one-third ($1/3$) of its original volume. Then add NH_4OH and $(NH_4)_2CO_3$ (never boil at this state.) Formation of white precipitate shows the presence of fifth group. Filter and wash the ppt. keep the filtrate for the radicals of sixth group. Dissolve the precipitate in least quantity of acetic acid and boil for a few minutes. Take a small part of this soln. and add. K_2CrO_4 soln. If a yellow ppt appears, heat the whole solution with excess of K_2CrO_2 so as to precipitate barium completely. If no ppt. appears on adding K_2CrO_4 soln, then do not add K_2CrO_4 solution to the whole soln. Now proceed as follows:

Residue: Yellow ppt. $BaCrO_4$. Ba^{++} (Barium) confirmed.	It may contain $(CH_3COO)_2$ and CH_3COO Ca. To it add $(NH_4)_2SO_4$ solution in excess and boil it filter it.	
	Filtrate: it may contain ca. to it add $(NH_4)_2C_2O_4$ soln. white ppt. Ca^{++} (calcium) confirmed.	Residue: White ppt. $(SrSO_4)$ Sr^{++} (strontium) confirmed.

Notes:

- (1) It is better to use saturated solution of $(NH_4)_2SO_4$ to detect Sr^{++} radical. After addition of the reagent, wait for few minutes to see if a precipitate of $SrSO_4$ is obtained.
- (2) Sometimes calcium does not get precipitated in its group due to the formation of $Ca(HCO_3)_2$ on addition of $(NH_4)_2CO_3$ to the concentrated filtrate of IVth group. As $Ca(HCO_3)_2$ is soluble and it passes into the filtrate of Vth group. Hence filtrate of Vth group must be tested for calcium before proceeding to VIth group.
- (3) They are tested in the order Barium, strontium, Calcium.

ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP

VI

Heat the fifth group filtrate with ammonium oxalate and discard the precipitate, if comes. Add 2-3 c.c. of NH_4OH and excess of sodium phosphate (Na_2HPO_4) to the filtrate. Shake the solution with a glass rod. After a few minutes a white crystalline precipitate results. Mg^{++} (Magnesium) confirmed.

Analysis of ammonium (NH_4^+) Radical (zero group)

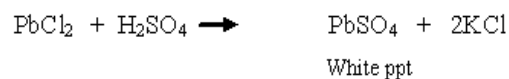
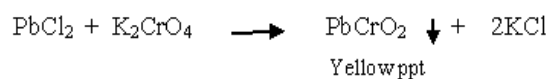
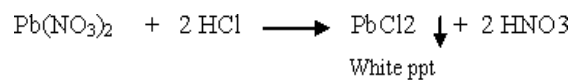
- (4) Heat a little mixture with 2-3 c.c $NaOH$ in a test tube. A characteristic smell of (NH_3) is obtained. On bringing a glass rod dipped in conc. HCl at the mouth of the test tube, enormous white fumes are produced.

- (5) On adding Nessler's reagent to the solution of the mixture → brown color of ppt. is obtained. This test is extremely sensitive and characteristic.

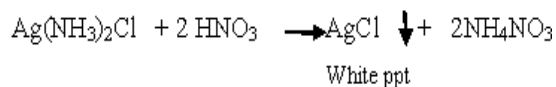
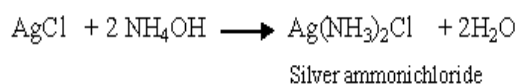
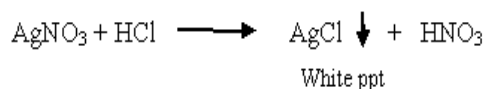
Note. Nessler's reagent is prepared by adding KI to Hg Cl₂ solution until the red ppt (HgI₂) formed, is dissolved. It is mixed with NaOH solution.

CHEMICAL REACTIONS INVOLVED IN THE TEST OF BASIC RADICALS

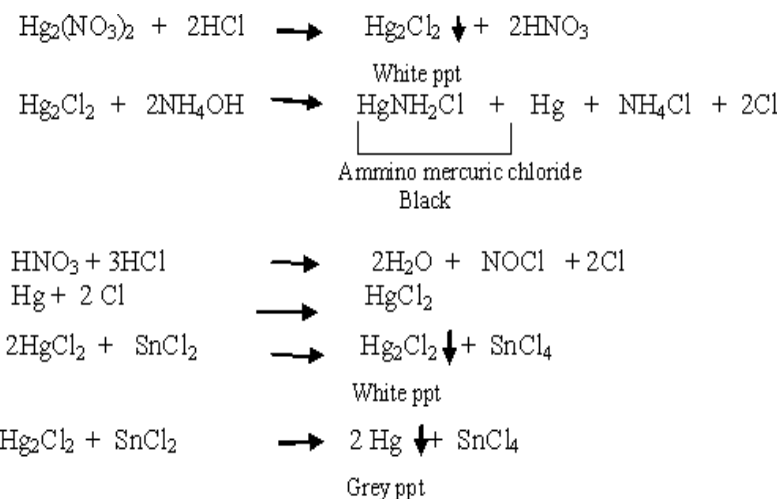
First Group: Lead (Pb⁺⁺), Silver(Ag⁺) Mercurous (Hg₂⁺⁺) and lead (Pb⁺⁺).



SILVER (Ag⁺) :

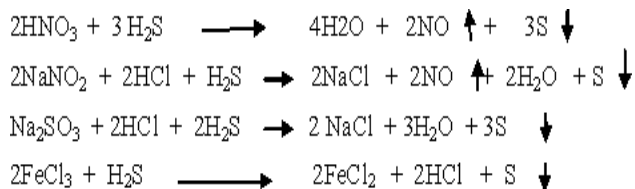


Mercurous (Hg⁺⁺):

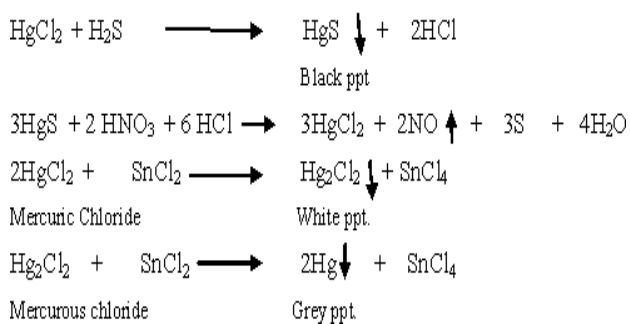


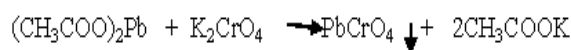
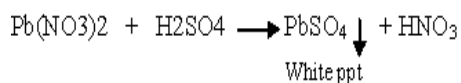
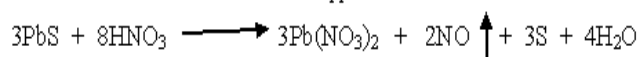
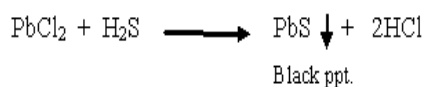
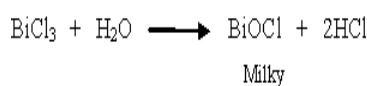
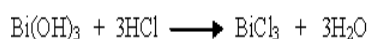
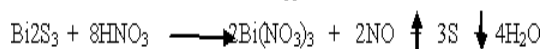
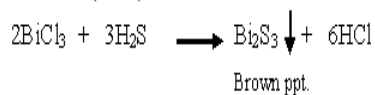
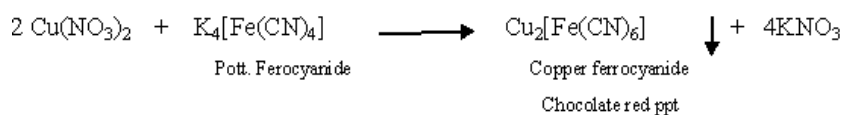
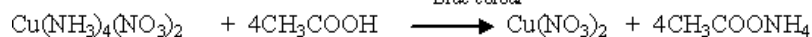
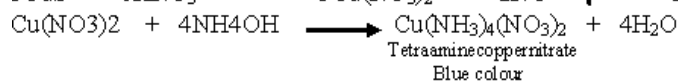
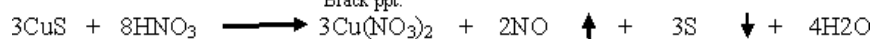
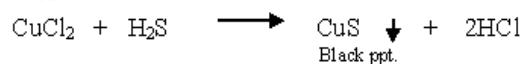
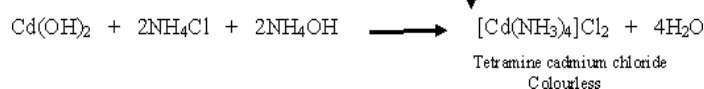
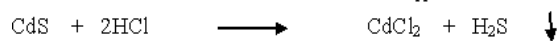
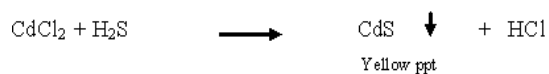
Second Group : Mercuric (Hg^{++}), Lead(Pb^{++}), Bismuth(Bi^{+++}), Copper(Cu^{++}), Cadmium(Cd^{++}), Arsenic(As^{+++}), Antimony(Sb^{+++}), Tin (Sn^{++} , Sn^{+++})

Sometimes, in second group, white or a light yellow ppt. is observed which is due to sulphur precipitated from H_2S by excess of HNO_3 or other oxidizing agents e.g. (NO_2^- , SO_3^- , Fe^{+++}). The ppt. should be rejected.

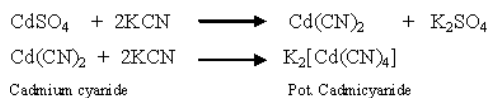
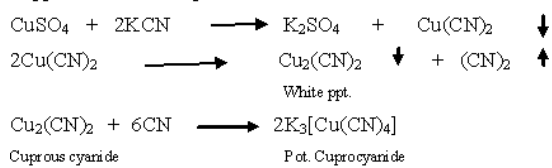


Mercuric (Hg^{++}):

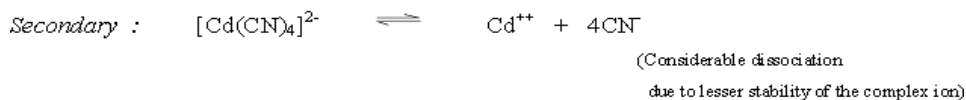
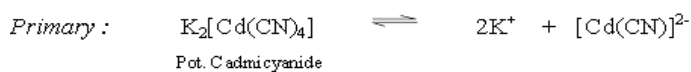
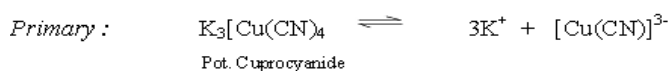


Lead (Pb⁺⁺) :**Bismuth (Bi⁺⁺⁺)****Copper (Cu⁺⁺) :****Cadmium (Cd⁺⁺):**

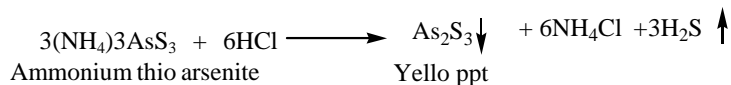
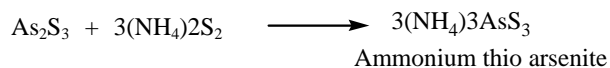
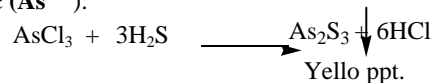
Copper-Cadmium Separation :



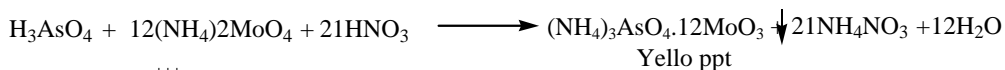
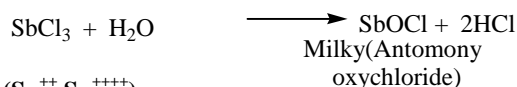
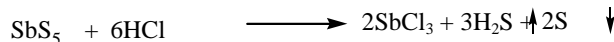
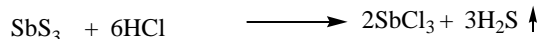
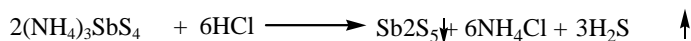
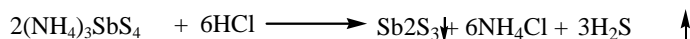
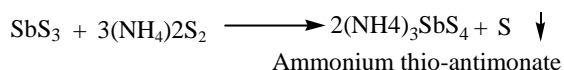
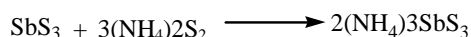
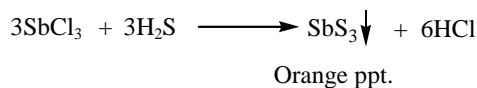
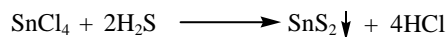
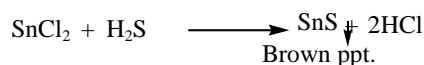
The complex of Cu and Cd dissociate as follows:



Thus when H₂S is passed through a solution containing these complexes, solubility product of CdS only is exceed and therefore it gets precipitated.

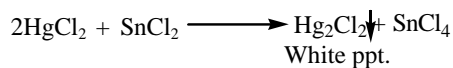
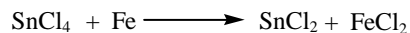
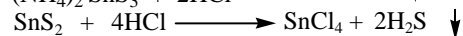
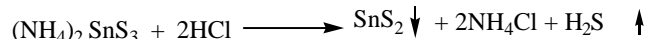
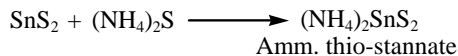
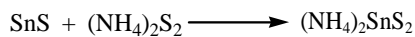
Arsenic (As⁺⁺⁺):

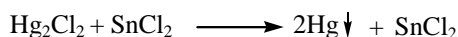
As₂S₃ dissolves in nitric acid forming arsenic acid(H₃AsO₄)

**Antimony (Sb⁺⁺⁺):****Tin (Sn⁺⁺, Sn⁺⁺⁺⁺):**

SnS- Insoluble in ordinary amm. sulphide but soluble in yello amm. sulphide.

SnS₂- Soluble in ordinary amm. sulphide



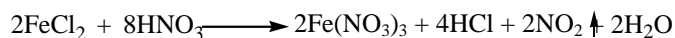


Third Group

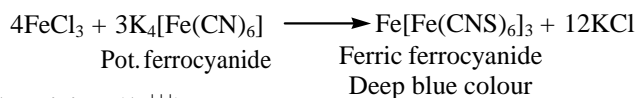
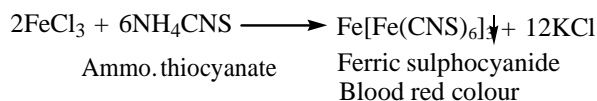
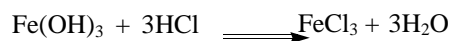
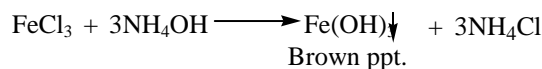
IRON, ALLMINIUM, CHROMIUM



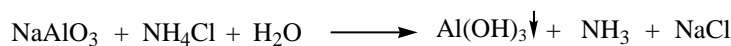
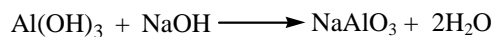
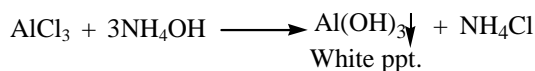
In the third group ferrous salts(Fe^{++}) are oxidized to ferric salts (Fe^{+++}) by boiling it with few drops of con. HNO_3 .



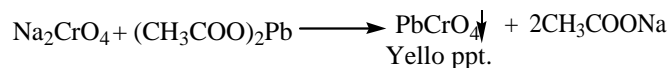
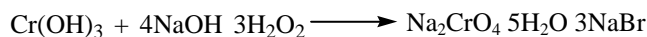
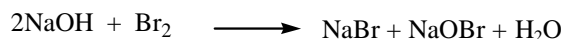
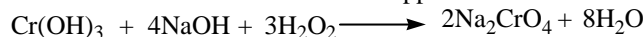
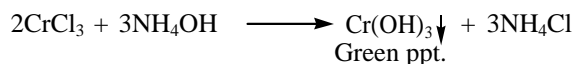
Iron (Fe^{+++}):



Aluminium (Al^{+++}):



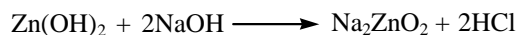
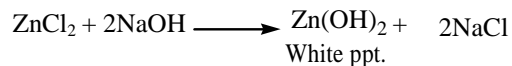
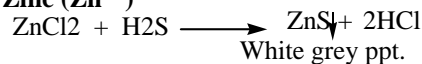
Chromium (Cr^{+++}):



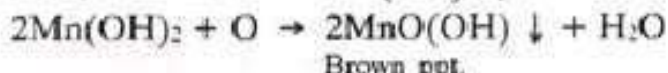
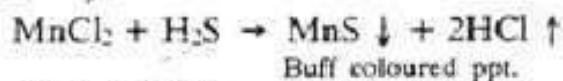
Fourth group

ZINC, MAGNESIUM, COBALT

Zinc (Zn^{++})

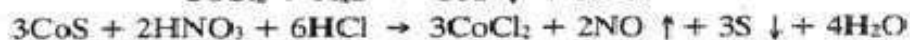


MANGANESE (Mn⁺⁺) :

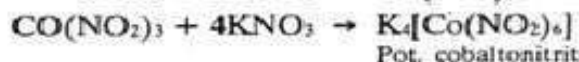


Pink colour
(Permanganic acid)

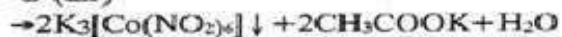
COBALT (Co⁺⁺) :



Aqua-regia



Pot. cobaltonitrite



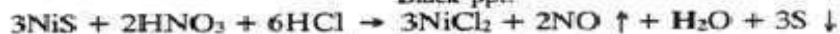
Yellow ppt.

Pot. cobaltinitrite

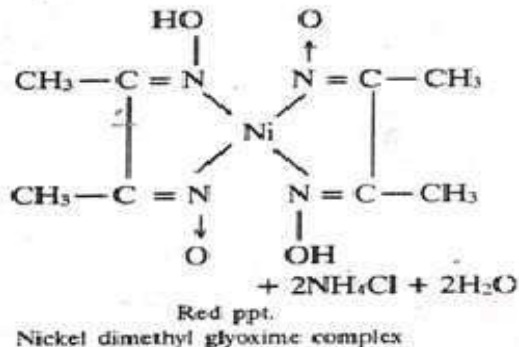
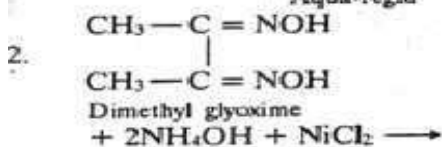
NICKEL (Ni⁺⁺) :



Black ppt.



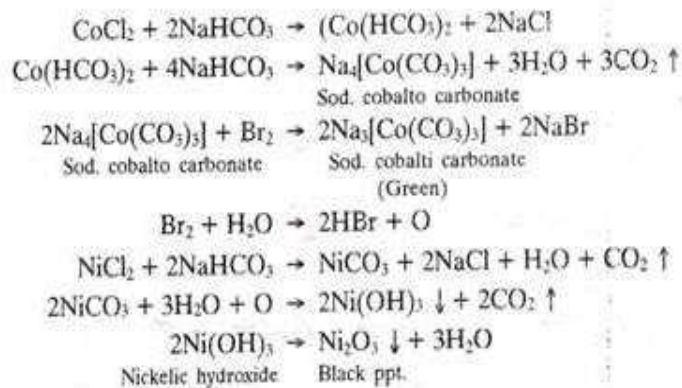
Aqua-regia



Test of Co and Ni with NaHCO₃-Br₂ water (Palit's test):

When the solution of cobalt and nickel salt is treated with excess of sodium bicarbonate, cobalt forms a pink coloured complex sodium cobalto-carbonate. Which on treated with bromine water is oxidised to green coloured sodium cobalti--carbonate. Nickel does not

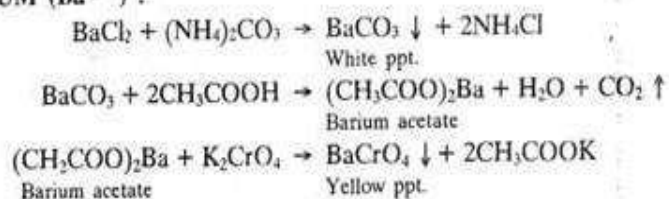
form a complex with NaHCO₃ but on heating with bromine water, it is oxidised to black nickelic oxide.



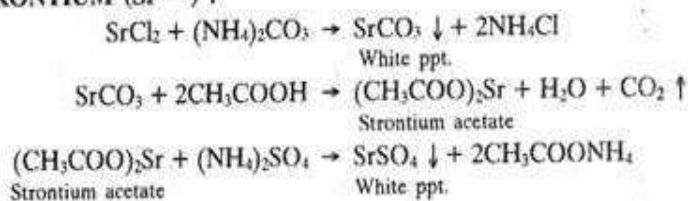
FIFTH GROUP

BARIUM, STRONTIUM, CALCIUM
(Ba⁺⁺, Sr⁺⁺, Ca⁺⁺)

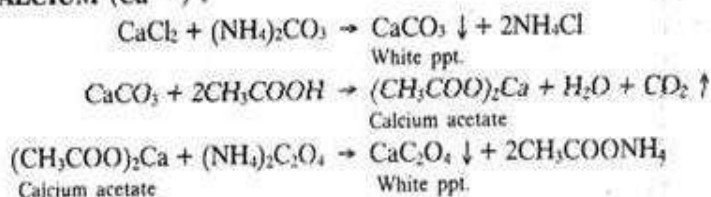
BARIUM (Ba⁺⁺) :



STRONTIUM (Sr⁺⁺) :



CALCIUM (Ca⁺⁺) :



Sixth group

Magnesium (Mg^{2+}):



zero group:

Ammonium (NH_4^+)

