Analytical Chemistry

Introduction

Chemistry deals with the study of numerous chemical compounds to understand the various applications of each compound in industry. Not only their uses but their process of development and their identification is very important. In the identification process of a chemical substance chemical analysis need to be done. The relevant subject that deals with systematic study in identification of chemical substance comes under the topic analytical chemistry.

Analytical chemistry is the science of obtaining, processing and communicating information about the composition and structure of matter. In other words, it is the art and science of determining what matter is and how much of it exists.

Analysis

The chemical compound can be basically analyzed in two ways-qualitatively as well as quantitatively. The substance being analyzed is known as analyte. Analysis is divided into two categories:

(i) Quantitative Analysis

(ii) Qualitative Analysis

- **Quantitative Analysis**

  In the quantitative analysis, the compound with respect to its quantity in a substance is analyzed. There are various methods to analyze a analyte quantitatively. The common methods used in quantitative analysis are volumetric analysis and gravimetric analysis.

  In volumetric analysis, the quantities of the constituents present in the given unknown solution are determined by measuring the volume of the solutions taking part in the given chemical reaction. It is a process by which the concentration or strength of a chemical substance is measured by measuring the volume of its solution taking part in a given chemical reaction. The main process of this analysis is called titration which means the determination of the volume of a reagent required to bring a definite reaction to completion.

  Gravimetric analysis is the quantitative measurement of an analyte by weighing a pure solid form of the analyte. Pure solids from solutions containing an unknown amount of a metal ion are obtained by precipitation. Since gravimetric analysis is an absolute measurement, it is a principal method for preparing and analyzing primary standards.

- **Qualitative Analysis**

  In the qualitative analysis, the compound is analyzed based on its chemical nature. The compound is identified as a gas, a salt or an ion. In qualitative analysis, the given compound is analyzed for the radicals, i.e., cation and the anion that it contains. Physical procedures like noting the colour, smell or taste of the substance have very limited scope because of the corrosive, poisonous nature of the chemical compounds. Therefore, what one has to resort to is the chemical analysis of the substance that has to be carried out along with the physical examination of the compound under consideration.

  Qualitative analysis mainly deals with

  (A) Identification of gases

  (B) Identification of salts

(A) Identification of gases

Based on the nature of the gas exhibited in a particular reaction. The other constituents of it can be identified.

Sr.No.	Gas	Characteristic of the gas
1.	Hydrogen	Colourless, odourless, neutral towards litmus, inflammable, bums blue in flame with pop sound
2.	Oxygen	Colourless, odourless, does not respond to litmus, non-Inflammable, supporter of combustion
3.	Chlorine	Greenish yellow in colour, suffocating odour, turns moist blue litmus paper red, turns moist KBr paper red, turns moist starch iodide paper black.
4.	Carbon dioxide	Colourless, odourless, turns moist blue litmus red, non-Inflammable, turns lime water milky.
5.	Hydrogen chloride	Colourless gas with pungent odour, turns moist blue litmus red, acidic.
6.	Sulphur dioxide	Colourless, with suffocating odour, turns blue litmus red, non-inflammable, turns acidified potassium dichromate solution to green.

7.	Hydrogen sulphide	Colourless, has rotten egg smell, turns moist blue litmus red, turns lead acetate paper black.

(B) Identification of Salts

A salt contains an anionic part and a cationic part. The common procedure for testing any unknown sample is to make its solution and then test this solution for the ions present in it. There are separate procedures for detecting cations and anions, therefore qualitative analysis is studied under anion analysis (or acid radicals) and cation analysis (or basic radicals). Before the chemical analysis, physical examination of salt is done. The physical examination of the unknown salt involves the study of colour, smell and taste. The test is not much reliable, but is certainly helpful in identifying some coloured cations. Characteristic smell helps to identify some ions such as ammonium acetate etc.

Physical Examination

Experiment	Observation	Inference
1. Colour	Blue or Bluish green Greenish Light green Dark brown Pink Light pink, flesh colour or earthy colour White	Cu^{2+} or Ni^{2+} Ni^{2+} Fe^{2+} Fe^{3+} Co^{2+} Mn^{2+} Shows the absence of $Cu^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Co^{2+}$
2. Smell Take a pinch of the salt between your fingers and rub with a drop of water	Ammoniacal smell Vinegar like smell Smell like that of rotten eggs	NH_4^+ CH_3COO- S^{2-}
3. Density	(i) Heavy (ii) Light fluffy powder	Salt of Pb^{2+} or Ba^{2+} Carbonate
4. Deliquescence	Salt absorbs moisture and becomes paste like	(i) If coloured, may be $Cu(NO_3)_2$, $FeCl_3$ (ii) If colourless, may be $Zn(NO_3)_2$, chlorides of Zn^{2+}, Mg^{2+} etc.

ACTIVITY CORNER

To test the presence of hydrogen sulphide gas in the given sample,

- **Material required:**
  Given sample, test tube, lead acetate paper.
- **Procedure:**
  Take the given sample in the test tube. Smell it. Now take a lead acetate paper and put it above the test tube.
- **Observation:**
  By smelling the sample, it gives the odour of rotten egg. The lead acetate paper also turns black.
- **Conclusion:**
- Smell of rotten egg and black colour of lead acetate paper confirms the presence of hydrogen sulphide gas.

To test the presence by nickel ion by physical examination of the salt

- **Discussion:**
  By seeing the colour of the salt we can detect the presence of Ni^{2+}. If the salt is greenish in colour it contains nickel ion (Ni^{2+}).

ILLUSTRATION

1. Give characteristic of hydrogen gas.

Sol. Hydrogen gas is colourless, odourless, neutral towards litmus, inflammable and burns in flame with pop sound.

2. Give two examples of deliquescent salt.

Sol. $Cu(NO_3)_2$, $FeCl_3$, $Zn(NO_3)_2$ and $MgCl_2$ etc.

3. Volumetric analysis is categorized under which analysis.

Sol. Volumetric analysis is based on the quantities of the constituents present in the known solution by measuring the volumes of the solution. Thus, it is categorized under quantitative analysis.

4. What is qualitative analysis?

Sol. Thy type of analysis that deals with the methods which are used to determine the constituents of a compound.

5. Qualitative analysis is for which type of salts.

Sol. Qualitative analysis is for inorganic salts.

6. What is the colour of iron salts?

Sol. Ferrous salts are usually light green while ferric salts are generally brown.

Identification of Anions

The common anions which we come across in salts include carbonate, sulphide, sulphite, chloride bromide, iodide, nitrate and sulphate. These anions or acid radicals are basically divided into 3 categories on the basis of the tests by which they can be identified.

- **First Group of Acid Radicals**

  The acid radicals involved in this group are carbonate (CO_3^{2-}), sulphide (S^{2-}), sulphite (SO_3^{2-}) and nitrite (NO_2^-). The group reagent is dilute sulphuric acid.

Experiment	Observation	Inference
Salt + dil. H_2SO_4	Effervescence or evolution of gases	1st group of acid radicals is present
	(a) Colourless, odourless gas turns lime water milky.	Carbonate (CO_3^{2-}) is confirmed.
	(b) Colourless gas with rotten egg smell and turns lead acetate paper black.	Sulphide (S^{2-}) is confirmed.
	(c) Colourless gas with suffocating smell. Heat and pass the gas through acidified $K_2Cr_2O_7$ solution. The solution turns green.	SO_3^{2-} is confirmed.
	(d) Colourless gas followed by brown gas and it turns ferrous sulphate solution black.	NO_2^- is confirmed.

- **Second Group of Acid Radicals**

  The acid radicals present in this group are chloride (Cl^-), bromide (Br^-), iodide (I^-) and nitrate (NO_3). The group reagent is concentrated sulphuric acid (H_2SO_4).

Experiment	Observation	Inference
Salt + conc. H_2SO_4 and heat (if necessary)	Effervescence with colourless or coloured gases	2nd group acid radical is present
	(a) Colourless gas with a pungent smell and gives dense white fumes when a glass rod dipped in ammonium hydroxide (NH_4OH) is exposed.	The acid radical may be Cl^-.
	(b) Brown gas evolves which intensifies on addition of MnO_2.	The acid radical may be Br^-.
	(c) Deep violet gas evolves.	The acid radical may be I^-.
	(d) Light brown gas evolves which intensifies on addition of copper turnings.	The acid radical may be NO_3^-.

- **Third Group of Acid Radicals**

  The acidic radicals involved in this group are sulphate (SO_4^{2-}), borate and phosphate.

Experiment	Observation	Inference
Aqueous solution of salt + dilute $HCl + BaCl_2$ solution	A white ppt. insoluble in dilute HCl is obtained.	Sulphate (SO_4^{2-}) is confirmed. $Na_2SO_4 + BaCl_2 \xrightarrow{H^+} \underset{White\ ppt.}{BaSO_4\downarrow} + 2NaCl$
Substance + 2mL conc. HNO_3 and heat, then add 2 mL ammonium molybdate + heat	Canary yellow precipitate is obtained.	Phosphate (PO_4^{3-}) is confirmed. $Ca_3(PO_4)_2 + 6HNO_3 \rightarrow 6Ca(NO_3)_2 + 2H_3PO_4$ $H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow \underset{yellow\ ppt.}{(NH_4)_3.PO_4.12MoO_3}$

ACTIVITY CORNER

To confirm the presence of chloride ion in the given salt sample.

- **Material required:**

  Given salt, test tube, conc. H_2SO_4, glass rod, NH_4OH solution.

- **Procedure:**

- Take salt solution in a test tube and add few drops of cone; H_2SO_4. Smell the evolved gas.
- Bring a glass rod dipped with NH_4OH solution near the mouth of the test tube.

- **Observation:**

  After adding conc. H_2SO_4 a colourless gas with a pungent smell is observed. When glass rod dipped with NH_4OH solution is brought near the mouth of test tube, dense white fumes are observed.

- **Conclusion:**

  Pungent odour and dense white fumes confirm the presence of chloride (Cl^-) in the salt.

ILLUSTRATION

7. A gas gives pungent odour with dilute H_2SO_4 .Can it contains sulphite anion?

Sol. We cannot surely say that the gas contains sulphite ions because NO_2^- also gives a pungent odour. Presence of sulphite ions can be confirmed by acidified $K_2Cr_2O_7$ paper. If the paper turns green it contains sulphite ions.

8. What are acidic and basic radicals?

Sol. Radicals carrying positive charge are called basic radicals and those carrying negative charge are called acidic radicals.

9. Why do inorganic salt ionize when dissolved in water?

Sol. Due to the high dielectric constant of water, the force of attraction holding the two ions in a salt decrease. Thus, the two ions separate. The ions are further stabilized by salvation.

10. Why a salt containing lead turns black in colour, when placed for a long time in laboratory?

Sol. Due to the formation of black lead- sulphide by the action of H_2S in atmosphere.

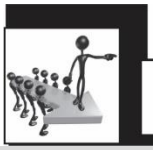
Identification of Cations

Salt also contains a cationic part (basic radical). Preliminary test such as dry heating test, charcoal cavity test, flame test and borax bead test may give us some indication about the cation present in the salt. However, the cation is finally detected and confirmed through a systematic analysis involving various tests. Before carrying out the tests for analysis of cation, the salt has to be dissolved in some suitable solvent to prepare its solution.

- **Flame Test**

  This is a specific test done for the detection of some cations which can impart colour to the flame.

Cation	Colour of the flame
Sodium	Golden yellow colour
Potassium	Lilac colour
Zinc	Green flashes
Barium	Apple green
Calcium	Brick red
Copper	Light green



Do You Know

- Acetic acid gives smell of vinegar but when added with alcohol gives a fruity smell of ester (organic compound).

- Charcoal cavity test is also used for detection of acid radicals.
- Borax bead test is performed only for coloured Salts

- **Test for Some Cations**

Cation	Addition of Reagent (Experiment)	Observation
NH_4^+	Salt + $NaOH$ + heat	Ammoniacal smell due to evolution of NH_3 gas. The gas gives white fumes when a glass rod dipped in dil. HCl brought near to the mouth of test tube. $NH_4Cl + NaOH \xrightarrow{\Delta} NaCl + H_2O + NH_3 \uparrow$ $NH_3 + HCl \rightarrow \underset{(white\ fumes)}{NH_4Cl}$
Pb^{2+}	Salt solution + dil. HCl	White ppt $Pb(NO_3)_2 + 2HCl \rightarrow \underset{(white\ ppt)}{PbCl_2}\downarrow + 2HNO_3$
Cd^{2+}	Salt solution + dil. $CH_3COOH + H_2S$ gas	Yellow ppt $CdCl_2 + H_2S \rightarrow \underset{(yellow\ ppt)}{CdS}\downarrow + 2HCl$
Al^{3+}	Salt solution + conc. $HNO_3 + NH_4Cl + NH_4OH$	White ppt $AlCl_3 + 3NH_4OH \rightarrow 3NH_4Cl + \underset{(white\ ppt)}{Al(OH)_3}\downarrow$
Fe^{3+}	Salt solution + conc. $HNO_3 + NH_4Cl + NH_4OH$	Reddish brown ppt $FeCl_3 + 3NH_4OH \rightarrow 3NH_4Cl + \underset{(raddish\ brown\ ppt)}{Fe(OH)_3}\downarrow$
Cu^{2+}	Salt solution + NH_4OH	Bluish ppt $Cu(NO_3)_2 + 4NH_4OH \rightarrow \underset{(blue\ ppt)}{[Cu(NH_3)_4][NO_3]_2} + 4H_2O$
Zn^{2+}	Salt solution + NH_4Cl + $NH_4OH + H_2S$ gas	Pale pink ppt $Zn(OH)_2 + H_2S \rightarrow \underset{(pink\ ppt)}{ZnS}\downarrow + 2H_2O$
Ca^{2+}	Salt solution + NH_4Cl + $NH_4OH + (NH_4)_2CO_3$	White ppt $CaCl_2 + (NH_4)_2CO_3 \rightarrow \underset{(white\ ppt)}{CaCO_3}\downarrow + 2NH_4Cl$

Do You Know

- H_2S gas is prepared in an apparatus known as Kipp's apparatus by using FeS pieces.
- Use of excess salt in borax bead test leads to the formation of opaque bead.
- We should never boil the salt with conc. H_2SO_4 as the acid may decompose to give SO_2 gas.

Activity Corner

To test the presence of aluminium cation in the given salt sample

- **Material required:**
  Salt, NH_4Cl, conc. HNO_3, NH_4OH, test tube.
- **Procedure:**
- Make a clear salt solution in the test tube by proper shaking. Now add conc. HNO_3 Cool the content. Now add solid NH_4Cl and excess of NH_4OH Solution. Observe the changes.
- **Observation:**

A white ppt is formed which settles at the bottom of the test tube.

- **Conclusion:**
  Formation of white ppt confirms the presence of aluminium ions in the salt

ILLUSTRATION

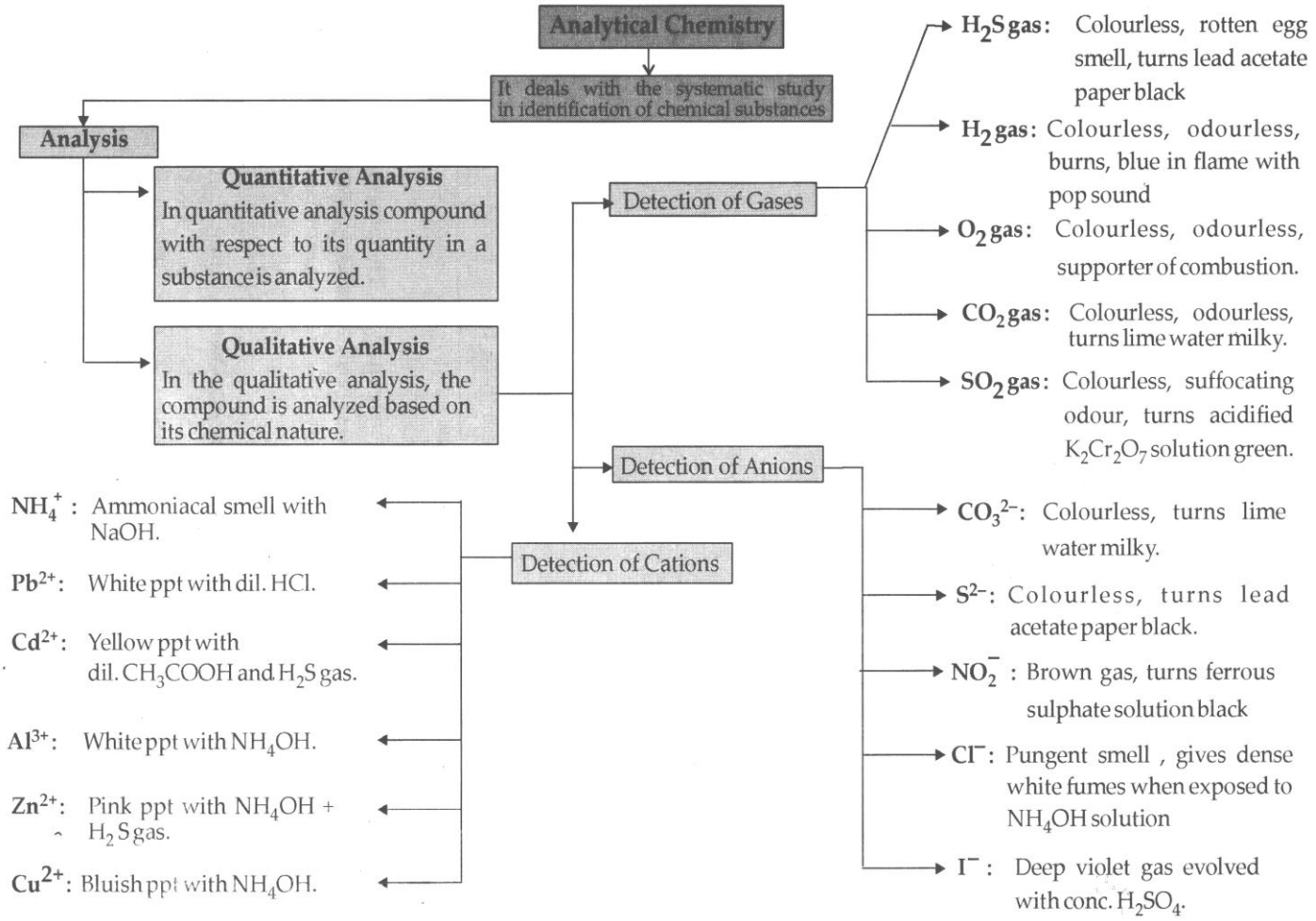
11. Can sodium hydroxide solution be used to distinguish between ferrous sulphate and ferric sulphate solution? If So, how?

Sol. Yes, on addition of sodium hydroxide solution to ferrous sulphate it forms a dirty green precipitate of ferrous hydroxide. On addition of sodium hydroxide solution to ferric sulphate it forms a reddish brown precipitate of ferric hydroxide.

12. Oil paintings turn blackish after sometime. What is the salt formed? Assume oil paint contains Pb^{2+}.

Sol. Oil paints containing lead (Pb^{2+}) ions turn black after sometimes because of formation of black lead sulphide.

CONCEPT MAP



Borax Bead Test

Borax is heated on a loop of platinum wire then colourless glassy bead of sodium metaborate and boric anhydride is formed.

$\underset{Broax}{Na_2B_4O_7.10H_2O} \longrightarrow Na_2B_4O_7 \longrightarrow \underset{sodium\ metaborate}{2NaBO_2} + \underset{boric\ anhydride}{B_2O_3}$ When boric anhydride reacts with coloured metallic salt, a characteristic colour bead of metal metaborate is formed.

e g., $CuSO_4 + B_2O_3 \longrightarrow \underset{Copper\ metaborate\ (blue)}{Cu(BO_2)_2} + SO_3$ Coloured metallic salts give different colour beads in different flames.

Colour of the bead		Inference
In oxidizing flame	In reducing flame	
1. Green when hot, light blue when cold.	Colourless when hot, opaque red when cold.	Cu^{2+}
2. Yellowish brown when hot, pale yellow when cold.	Green, hot and cold.	Fe^{2+} or Fe^{3+}
3. Amethyst (pinkish violet) in both hot and cold.	Colourless, hot and cold.	Mn^{2+}
4. Brown when hot, pale brown when cold.	Grey or black when hot and opaque when cold.	Ni^{2+}
5. Deep blue in both hot and cold.	Deep blue in both hot and cold.	Co^{2+}

Titration

- The main process or important step in volumetric analysis. The process of titration is employed of find out the volume of one solution required to react completely with a certain known volume of solution of some other substance. In other words, determination of strength of one solution using another solution of known strength under volumetric conditions is known as titration.
- The substance added to the analyte in a titration is known as titrant. End point plays an important role in the titration. It is the point where reaction between two solutions is just completed or the point in a titration at which the quantity of titrant is exactly sufficient for stoichiometric reaction to be completed with the analyte. At this point there is a sudden change in physical properties such as indicator colour, pH, conductivity or absorbance.
- Thus, titration is a general class of experiments where a known property of one solution is used to determine unknown properties of another solution. There are various types of titrations viz., acid-base titration, oxidation-reduction titration, iodine titration, complex metric titration etc.