Chemical analysis

Qualitative analysis

Quantitative analysis

(1) Qualitative analysis means to finding (identification and number) of the components in different solutions or mixtures

For example finding abnormal components in the biological fluids (urine , blood , ….. etc.)

(2) Quantitative analysis means to finding the exact quantity of the substance in different solutions or mixtures.

For example finding the exact amount of uric acid in the serum.

(1-1) Separation and Detection for Cations

Separation of cations involve removal of one or more cations from mixture by formation of insoluble precipitates. The groups of reagents used for classification of most common cations with respectively are :

1- dil. HCl
2- H_2S in acidic medium
3- $(NH_4)_2S$ in neutral medium
4- $(NH_4)_2CO_3$ in neutral medium

The classification is based on whether a cation reacts with these reagents by formation a precipitate or not .

The cations are distributed into five groups

Groups	Precipitant factor	Cations
Group I	dil. HCl	Pb^{+2} , Hg^{+} , Ag^{+}
Group II	H_2S in acidic medium	Hg^{+2} , Cu^{+2} , Bi^{+3} , Cd^{+2} , Sn^{+2} , Sn^{+4} As^{+3} , As^{+5}
Group III	$(NH_4)_2S$ in neutral medium	Co^{+5} , Fe^{+2} , Cr^{+3} , Al^{+3} , Zn^{+2} , Mn^{+2} , Ni^{+2}
Group IV	$(NH_4)_2CO_3$ in neutral medium	Ca^{+2} , Sr^{+2} , Ba^{+2} , Mg^{+2}
Group v	No precipitant factor	Na^{+} , K^{+} , NH_4^{+} , Li^{+} , H^{+}

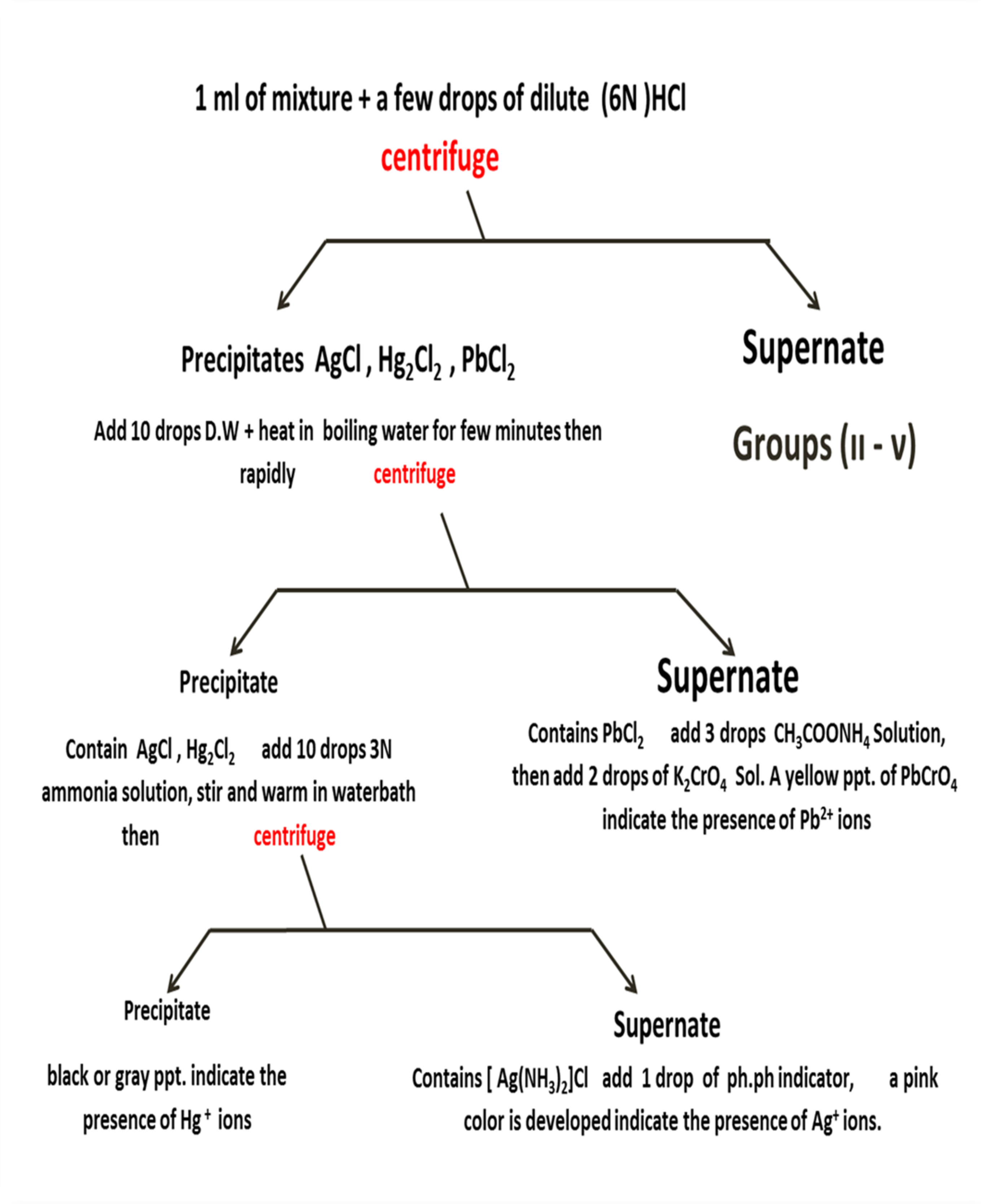
The caions of group I are provided as nitrate : $AgNO_3$, $Hg_2(NO_3)_2$, $pb(NO_3)_2$ and precipitated as chlorides AgCl , Hg_2Cl_2 , $PbCl_2$ according to the following equations

$$AgNO_3 + HCl \longrightarrow AgCl + HNO_3$$

$$Hg_2(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 + 2HNO_3$$

$$Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2 + 2HNO_3$$

The experiment / to analysis a mixture which contain cations of group I and test for cations of this group we should follow the next diagram



1 ml of mixture + a few drops of dilute (6N)HCl

centrifuge

Precipitates AgCl , Hg_2Cl_2 , $PbCl_2$

Add 10 drops D.W + heat in boiling water for few minutes then rapidly centrifuge

Supernate

Groups (II - V)

Precipitate

Contain AgCl , Hg_2Cl_2 add 10 drops 3N ammonia solution, stir and warm in waterbath then centrifuge

Supernate

Contains $PbCl_2$ add 3 drops CH_3COONH_4 Solution, then add 2 drops of K_2CrO_4 Sol. A yellow ppt. of $PbCrO_4$ indicate the presence of Pb^{2+} ions

Precipitate

black or gray ppt. indicate the presence of Hg^+ ions

Supernate

Contains $[Ag(NH_3)_2]Cl$ add 1 drop of ph.ph indicator, a pink color is developed indicate the presence of Ag^+ ions.

Results

Cation	**dil. HCl**	Detection	**Conclusion**
Pb^{+2}	**White ppt.**	Yellow ppt.	**Indicate the presence of Pb^{+2} ions**
Hg^{+}	**White ppt.**	Black ppt.	**Indicate the presence of Hg_2^{+2} ions**
Ag^{+}	**White ppt.**	Pink color	**Indicate the presence of Ag^{+} ions**

Notes

- **The solid precipitate and the liquid are separated by either filtration or by centrifugation**
- **In this experiment , centrifugation will be used for separations**
- **In this technique, the mixture is centrifuged at high speed in a small tube**

- **To avoid severe and possibly dangerous vibration of the centrifuge the tubes must always be balanced by placing a tube similarly weighted with liquid (for example water) in the holder directly opposite the first tube**

- **Cations of groups I are precipitated as insoluble chlorides $PbCl_2$, AgCl , Hg_2Cl_2 while chlorides of all other common cations are soluble**

- **AgCl is soluble in aqueous ammonia forming soluble complex $[Ag(NH_3)_2]Cl$**

- **Cations are the positive part of any salt**

- **The addition of water with heating and stirring to dissolve the Pb^{+2} ions and leave the Ag^{+} and Hg_2^{+2} ions as precipitates .**

- **The addition of NH_4OH to dissolve the Ag^{+} ions and precipitate the Hg_2^{+2} ions as black ppt. .**

- **The addition of phenolphthalein indicator , to indicate the presence of Ag^{+} ions .**

(2) QUANTITATIVE ANALYSIS

According to measuring way we can classify quantitative analysis to

1- Classical methods

   A- Gravimetric methods

   B- Volumetric methods

2- Instrumental methods

Volumetric Methods

Titrimetric Methods :- One from **volumetric methods** means to finding the exact quantity of substance by using **titration**.

Titration **:-** The process of addition of standard solution with known concentration which called titrant to the unknown which called analyte , we can know the end point of this process by using **the indicators**.

Indicators **:-** They are **complex organic** compounds that exist in two different color forms which depend upon whether they are in acid or base or neutral medium. For example methyl orange is yellow in alkaline or neutral conditions but it is red in acidic condition.

The first change in color of indicator means the **end point** of the reaction which used in the calculation.

There are four types of titration

1- Acid-Base (Neutralization) reaction

2- Precipitation reaction

3- Oxidation-Reduction (Redox) reaction

4- Complex formation reaction

1- ACID-BASE TITRATION

Acid-Base Titration means complete reaction between acid and base to form salt and water

$$2\ HCl + Na_2CO_3 \longrightarrow H_2CO_3 + 2\ NaCl$$

$$H_2CO_3 \longleftrightarrow H_2O + CO_2$$

Because of (HCl) consider a **secondary** standard solution we must titrate with a known concentration of a primary standard solution of Na_2CO_3 and this process called **Standardization** of HCl solution .

STANDARDIZATION OF HCL SOLUTION

The concentrated HCl is about (11-12) Molar and cannot used as primary because its volatility so it must be titrated against a primary standard solution according the next steps.

1- Fill the graduated burette with HCl solution.

2- put 5 ml of Na_2CO_3 solution in clean conical flask then add (1-2) drops of methyl orange as indicator to Na_2CO_3 , the color becomes yellow

2- Titrate with HCl solution until the color becomes red

3- Use the relationship { $N_1 \times V_1$ (HCl) $= N_2 \times V_2$ (Carbonate) } and from this relationship find Normality for HCl

4- Use Normality of HCl to find the unknown concentration of carbonate by applying {$N_1 \times V_1$ (HCl) $= N_2 \times V_2$ (Carbonate) } with repeating the previous steps

Result and calculation :-

$$N = \frac{\text{No. of equivalent of solute}}{\text{Volume of solution (liter)}} \qquad \ldots(1)$$

or

$$N = \frac{\text{No. of miliequivalent of dissolved solute}}{\text{Volume of solution (milliliter)}} \qquad \ldots(2)$$

$$\text{No. of equivalent} = \frac{\text{weight}}{\text{Equivalent wt.}} \qquad \ldots(3)$$

$$\text{No. of milliequivalent} = \frac{\text{weight} \times 1000}{\text{Equivalent wt.}} \qquad \ldots(4)$$

$$\text{Equivalent wt.} = \frac{\text{Molecular wt.}}{\text{ŋ}}$$

$$N = \frac{\text{wt.}}{\text{equivalent wt.} \times V\ (\text{liter})} \quad \text{or} \quad N = \frac{\text{wt.} \times 1000}{\text{equivalent wt.} \times V\ (\text{ml})}$$

$$N = \frac{\text{weight} \times 1000}{\text{equivalent wt.} \times V\ (\text{ml})}$$

$$\text{equivalent wt. of } Na_2CO_3 = \frac{\text{molecular wt.}}{\text{ŋ}}\ ; = \frac{106}{2} = 53$$

.

$$N = \frac{\text{wt.} \times 1000}{\text{equivalent wt.} \times V\ (\text{ml})} = \frac{0.5 \times 1000}{53 \times 100} = 0.094\ N \text{ of } Na_2CO_3$$

From the following relationship find the normality of HCl

$$\begin{array}{ccccc} \text{HCl} & & & Na_2CO_3 & \\ N_1 \times V_1 & = & N_2 & \times & V_2 \\ ? \times \text{read on burette} & = & 0.094 & \times & 5 \end{array}$$

$N_1 = y$ (the normality of HCl)

Then find the conc. of the unknown Na_2CO_3 in gm./100 ml from the normality of HCl

$$\begin{array}{ccccccc} & \text{HCl} & & & \text{Na}_2\text{CO}_3 & \\ N_1 & \times & V_1 & = & N_2 & \times & V_2 \end{array}$$

↓

y × read on burette = **?** × 5

Finally find the weight of the unknown Na_2CO_3 which dissolved in 100 ml. in D.W. from

$$N = \frac{wt. \times 1000}{53 \times 100}$$

wt. = …… gm./ 100 ml. of Na_2CO_3

Notes

- Normality :- Normality is the unit to measure the concentration of the solution.
- Equivalent point :- The point at which amount of the standard solution equivalent to the substance that react during titration .
- Indicators :- Complex organic compounds that change the color with change the pH .

- Conditions of the initial standard materials

1. The material has a known structure and is easy to obtain with a high degree of purity or easy to purify it after detection or to identify the impurities it contains, so that it does not exceed (0.1 - 0.2 %).
2. The substance is non-hygroscopic and should not be altered during the weight process
3. The material shall be easily soluble in water under the conditions in which it is used.
4. Their equivalent weight must be large until weight errors become negligible.

5. The primary standard material solution shall not be colored before or after the calibration to avoid color interference with the color of the manual used to find the reaction point.
6. They should not be affected by light, temperatures, dust, and organic matter.

- Primary standard solution :-

1) High purified chemical compound and stable for a few months .
2) The interaction between the standard solution and the material to be evaluated should be rapid.
3) The interaction is complete and non-inverse and necessary to obtain a clear parity point.
4) The possibility of expressing interactions with balanced chemical equations.
5) The standard solution detector gives a clear equivalent point.

Oxidation – Reduction (Redox) Reaction

Redox reaction is a chemical reaction involves the transfer of electrons from an atom and gain of these electrons by another atom.

Potassium permanganate ($KMnO_4$) is a powerful oxidizing agent, which was first introduced into volumetric analysis specifically in titrate with Fe^{+2} .

In acid solution , $KMnO_4$ reduce according to the following equation :

$$MnO_4^{-} + 8H^{+} + 5e^{-} \longrightarrow Mn^{2+} + 4H_2O$$

From this equation notice that the oxidation number of the manganese change from +7 to +2 , then the change in oxidation no. is (5) and therefore, the equivalent weight equal (158.03 ÷ 5 =31.606) .

While ferrous ions which severe from oxidized according to the following equation :

$$Fe^{2+} - e^{-} \longrightarrow Fe^{3+}$$

Then the final equation for oxidation and reduction is

$$MnO_4^{-} + 8H^{+} + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

It follows that the equivalent weight of $KMnO_4$ is one-fifth of the molecular weight.

H_2SO_4 is the most suitable acid, as it has no action upon the permanganate.

While if we use HCl there is likelihood of the reaction :

$$2\ MnO_4^- + 10\ Cl^- + 16\ H^+ \longrightarrow 2\ Mn^{2+} + 5\ Cl_2 \uparrow + 8\ H_2O$$

Potassium permanganate ($KMnO_4$) acts as reversible indicator for end point titration .It is secondary standard solution and if it is used it must be titrated with a primary standard solution (reducing agent) such as $Na_2C_2O_4$ according to the equations.

$$2\ Na^+ + C_2O_4^{2-} + 2\ H^+ + SO_4^{2-} \longrightarrow H_2C_2O_4 + 2\ Na^+ + SO_4^{2-}$$

$$5\ H_2C_2O_4 + 2\ MnO_4^- + 6\ H^+ \longrightarrow 10\ CO_2 + 2\ Mn^{2+} + 8\ H_2O$$

Preparation and Titration of $KMnO_4$ solution

Procedure:

1- Weight approximately about 0.3 g of $KMnO_4$.

2- Dissolve it in 80 ml of D.W. and heat the solution till boiling, cool , filter the solution if necessary then transfer it to a volumetric flask 100 ml and complete it till to mark.

3- Fill the burette by $KMnO_4$ solution.

4- Weight exactly 0.67 g of $Na_2C_2O_4$ (primary standard) , dissolve it in D.W. and dilute the solution to 100 ml in volumetric flask.

5- Pipette 5 mL of $Na_2C_2O_4$ in a conical flask add 10 mL of 3N H_2SO_4 and heat the solution in the water bath until 60 °C

6- Titrate the solution rapidly while it is hot with $KMnO_4$ solution until the permanent faint pink color is produced.

7- Repeat the process of titration two times then find the exact concentration of $KMnO_4$ using the following relationship:

$N \times V\ (KMnO_4) = N \times V\ (Na_2C_2O_4)$

Calculation :

The equivalent weight of sodium oxalate is 67

1 ml 1N $KMnO_4 \equiv 0.067$ g $Na_2C_2O_4$

or

$$\text{equivalent wt. of } Na_2C_2O_4 = \frac{\text{molecular wt.}}{2}\ ;\ = \frac{134}{2} = 67$$

.

$$N = \frac{\text{wt.} \times 1000}{\text{equivalent wt.} \times V\text{ (ml)}} = \frac{0.67 \times 1000}{67 \times 100} = 0.1\text{ N of } Na_2C_2O_4$$

From the following relationship find the normality of $KMnO_4$

$$\underset{KMnO_4}{N_1 \times V_1} = \underset{Na_2C_2O_4}{N_2 \times V_2}$$

? × read on burette = 0.1 × 5

$N_1 = y$ (the normality of $KMnO_4$)

Then find the conc. Of the unknown $Na_2C_2O_4$ in gm. / 100 ml from the normality of $KMnO_4$

$$\underset{KMnO_4}{N_1 \times V_1} = \underset{Na_2C_2O_4}{N_2 \times V_2}$$

y × read on burette = **?** × 5

Finally find the weight from $Na_2C_2O_4$ which dissolved in 100 ml. in D.W.

$$N = \frac{\text{wt.} \times 1000}{67 \times 100}$$

wt. = …… gm./ 100 ml. of $Na_2C_2O_4$

Notes

1- Solution of $KMnO_4$ should not allowed to stand in the burette for longer time because it decomposes to MnO_2 (brown ppt.)

2- During the titration , if addition of $KMnO_4$ is too rapid some MnO_2 will be produced in addition to Mn^{2+} which appears as brown coloration of the solution