D.N.R.COLLEGE (AUTONOMOUS): BHIMAVARAM
DEPARTMENT OF PG CHEMISTRY

TRADITIONAL METHODS OF ANALYSIS – II

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UNIT-I

PRECIPITATION METHODS-I

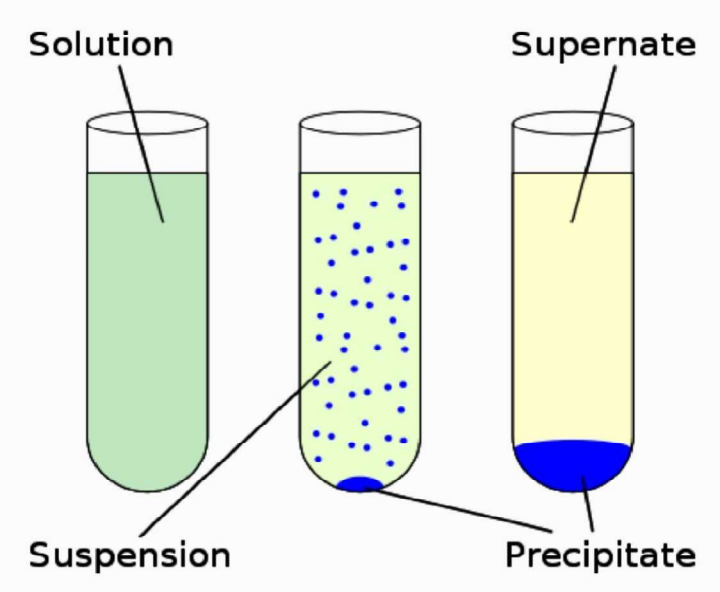
a) Precipitation methods:-

Precipitation is a technique used to separate a mixture based on the solubility of its components. The solubility of a compound depends on the ionic strength of the solution, its pH, and temperature. A dissolved compound can be precipitated out of solution by introducing a counter ion.

Precipitation:-

Here the quantitative determination of analyte (Cl, Br, I-) by forming a precipitate by addition of suitable reagent (or) solvent to the analyte to is called precipitation.

Precipitation involves the conversion of a substance in solution phase to solid phase by the addition of a suitable reagent for satisfactory precipitation the following requirements are to be the desired substance must be quantitatively precipitated. If the method is employed for quantitative determinations the weight form of the precipitate should be staichiometric compound of known composition. The precipitate must be free from impurities and should be easy filter.



Crystal habit and super saturation:-

Crystallization:-

Crystallization is the spontaneous arrangement of the particles repetitive orderly, i.e., regular geometric patterns.

Crystal:-

A Crystal can be defined as a solid particle, which is formed by solidification (crystallization) process (under suitable environment) in which structural units are arranged by a fixed geometric pattern or lattice.

Crystal Habit:-

Crystal habit is a description of the shapes and aggregates that a certain mineral is likely to form.

Crystal Habit:-

The relative sizes of the faces of a particular crystal can vary considerably. This variation is called a modification of habit.

The crystals may grow more rapidly, or be stunted, in one direction; thus an elongated growth of the prismatic habit gives a needle shape crystal (acicular habit) and a stunted growth gives a flat plate like crystal (tubular, platy or flaky habit).

Nearly all manufactured and natural crystal is distorted to some degree, and this frequently leads to a misunderstanding of the term "symmetry".

Perfect geometric symmetry is rarely observed in crystals, but crystallographic symmetry is readily detected by means of a goniometric. The relative growths of the faces of a crystal can be altered, and often controlled, by a number of factors.

Rapid crystallization, such as that produced by the sudden cooling or seeding of a supersaturated solution, may result in the formation of needle crystals; impurities in the crystallizing solution can stunt the growth of a crystal in certain directions; and crystallization from solutions of the given substance in different solvents generally results in a change of habit.

The degree of super saturation or super cooling of a solution or melt often exerts a considerable influence on the crystal habit, and so can the state of agitation of the system.

Super saturation:-

Solubility:-

The amount of substance can be dissolved in the given weight of the solvent should be equilibrium with the solvent.

Saturation solution:-

The maximum amount of substance can be dissolved in given solvent weight of the solvent that should be equilibrium with the solvent.

Super saturated Solution:-

If the amount of substance dissolved in a solvent is more than the equilibrium solubility that is called super saturated solvent. It is highly & Meta stable & it is readily precipitate.

$$MA \rightarrow M^{+} + A^{-}$$

$$K = [M^{+}]\,[A^{-}] / [MA]$$

Mechanism of precipitate:-

The precipitation of solid AB solution occurs when its solubility product is exceeded. The ions A^{+} & B^{-} come together forming a crystal lattice which grows sufficiently large to settle to bottom.

During the growth processes the particles passes through colloidal stage with a particle diameter 10^{-7}-10^{-4}cm.

The processes can be represented as.

Ion in solution→ Colloidal particles → Precipitates

10^{-8}cm→10^{-7}-10^{-4}cm→>10^{-4}cm

Nucleation and crystal growth:-

Crystal formation or precipitation Formation:-

Two steps are involved in the formation of precipitate.

i) Nuclei formation

ii) Crystal growth

i) Nuclei formation:-

The first step in the precipitation is the formation of very Small particles is called nuclei. These can be classified in to two types.

A) Homo nucleation

B) Hetero nucleation

A) Homo nucleation:-

The process of the Formation of homogeneous nuclei is called homogeneous nucleation.

In homogeneous nucleation is as same type of ions as that of the main precipitate.

The homogeneous nucleation results in the form of colloidal precipitation. This type of nucleation is possible at super saturation occurs immediately.

In case of homogeneous nucleation large no. of small size particles are formed. Due to the formation of small particles the Filtration of particles very difficult in the filtration process and the surface area of the particles increase it helps the increasing the adsorption properties of the impurities on the main precipitate.

B) Heterogeneous nucleation:-

This type of nucleation is included by extraneous materials. Here such as foreign materials in the reaction of the solutions (or) Impurities of the walls of the containers.

It leads to the Formation of if no of new particles. This number is equal to the foreign nuclei accidently present. In this type of nuclei formation of possible only at relative small super saturation.

In case of heterogeneous nucleation small no. of large particles are formed due to the formation of large particles filtrate property becomes easy and due to the formation of large particle the surface area of the particles decreases then the adsorption of the particle decreases. Here pure precipitate is obtained from heterogeneous nucleation.

ii) Crystal growth:-

The crystal growth involves disposition of cations & anions stable nuclei. i.e,

$$\text{Nucleus} + \text{ions} \rightarrow \text{Crystal growth}$$

Crystal growth is not a simple process; it is second process in the precipitation process.

The primary requirement for the crystal growth is nuclei formation. Crystal growth rate is determined by diffusion lattices ions to the surface.

The kinetics of crystal growth is first order with respective to the conc. of ions (or) super saturation.

The rate of growth is found to be directly proportional to the super saturation and can be a expressed as,

$$R.G \alpha A (Q-S) = KA (Q-S)$$

Where,

K= Constant

A= Surface area of the exposed solid

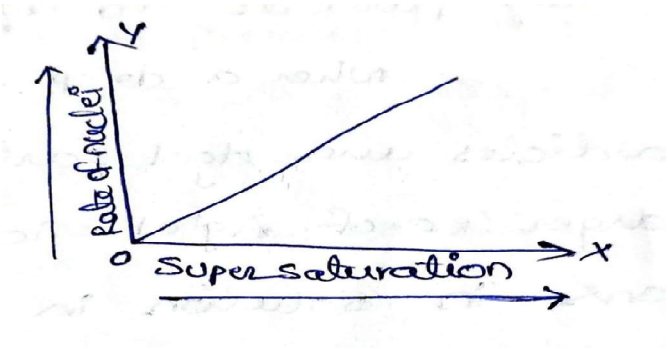
The rate of nucleation is depends up on the degree of Super Saturation. Nucleation increases essentially with super saturation.

$$\text{Rate of nucleation } \alpha (Q-S)\ x$$

$$\text{Rate of nucleation} = K (Q-S)\ x$$

X, E constant and x>1

The plot shows at low super saturation. So the nuclei rate is zero. At highly super saturated state rapid nuclei formation is observed.



A/C to Von Weimar theory to explain,

Here the super saturation in an important role in determining the particle size in precipitate. He has introduced that the velocity of the precipitation formation is depends up on the Q-S/S.

$$\text{Rate of precipitation} = K [Q-S/S]$$

Where, 'Q' is the total cone of the Substance to the precipitated from the solution. 'S' is the solubility of the crystals of microscopic size and 'K' is a constant. The term (Q-S) represented the degree of super saturation at the moment.

The precipitation begins the larges, the larger this term the more rapid is the growth of the particles. i.e.; the grater is the no. of nuclei forms.

The 'S' in the denominator represent the force resistant then the precipitate (or) causing the precipitate to re dissolve.

Here the grate greater value of `S' the smaller will be ratio & consequently, The Smaller No. of nuclei is formed. We are interested in obtained large precipitated particles. We should aim at adjusting the (Q-S) as lowest possible.

Solubility and particle size:-

Solubility:-

Solubility is the ability of a solid, liquid, or gaseous chemical substance (referred to as the solute) to dissolve in solvent (usually a liquid) and form a solution. Solubility does not depend on particle size; given enough time, even large particles will eventually dissolve. The degree of which a substance is dissolves in a solvent to make a solution (usually expressed as grams of solute per liter of solvent).

Factors affecting solubility:-

Temperature, basically, solubility increases with temperature, polarity. In most cases solutes dissolve in solvents that have a similar polarity, pressure, solid and liquid solutes, and molecular size. Stirring increases the speed of dissolving.

Particle size:-

The particle size of the solids also affects its solubility in a given solvent. Generally, a decrease in the particle size causes an increase in the solubility. This is because a decrease in particle size results in increase in surface area and surface free energy which increases solubility. In a collection of particles of more than one size, two properties are important, namely.

1. The shape and surface are of the individual particles.

2. The particle size and size distributions (The size range and number or weight of particles).

Any collection of particles is usually poly disperse. It is therefore necessary to know not only the size of a certain particle, but also how many particles of the same size exist in the sample. Thus, we need an estimate of the size range present and the number or weight fraction of each particle size. This is the particle-size distribution and from it we can calculate an average particle size for the sample.

Common methods of particle size measurement sieves. While this is an old technique, it has the advantage of being cheap and particularly useful for the measurement of large particles, sedimentation. This has been a common method used (historically) in clay and ceramics industries, electro zone testing, and laser diffraction.

Colloids:-

Colloidal particles have large surface area consequently adsorption property of the particles increases in the colloidal state. I.e., means the surface tends to adsorb other ions from the solution causing particles to acquire in an electric charge.

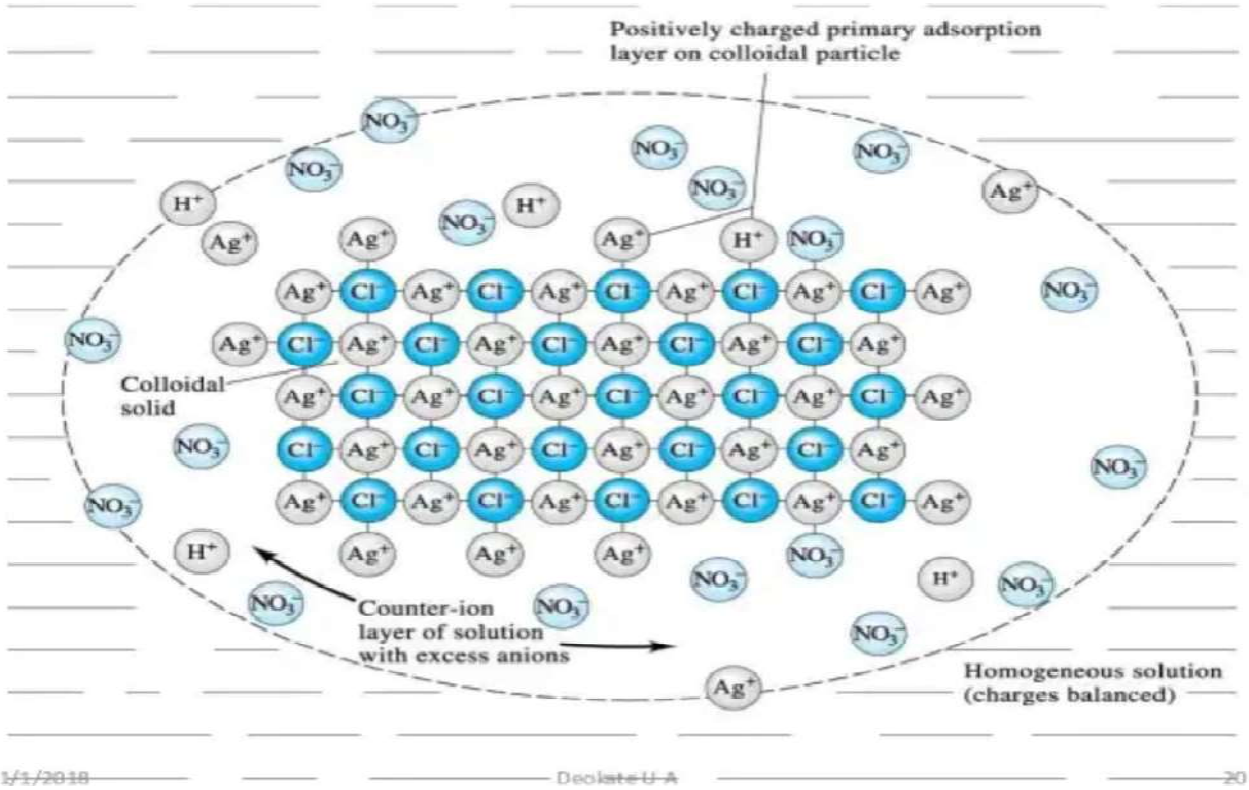
When a drop of silver nitrate is added to NaCl & AgCl Particles and particles grow to colloidal dimension. They are larger no. of Ag^+ Cl^- ions on the surface & Na^+ Cl^- ions & NO_3^- ions in solution in this solution the ion Cl^-.

Thus The Surface of the particles adsorbs a large no. of chloride ions causing the particles to be negatively charged. The chloride ions from the primary layer attract the Na^+ ions forming a secondary layer, which is held more loosely.

These particles are made to coagulate & from large particles by removal of charges into the primary layer. In this case AgCl this is achieved by the further addition of silver nitrate until equality amount of Ag^+ Cl^- are formed.

The Ag^+ ions are more strongly attracted to the primary layer of Cl^- ions.

Then the Na^+ ions causing the replacement of the later in the secondary layer and neutral the negative charge, due to primary layer, when this occur the particles aggregative size large enough to setting from solution. This process is called coagulation.



When coagulation of colloids occurs coagulating out dragged down with precipitate, when the precipitate is washed with distilled water continuously. These ions are removed from the solid particles causing then go back into colloidal dimension and passes through the filter paper such process is called peptisation. This has to be avoided in quantitative precipitate a volatile electrolyte is added to the working solution, this electrolyte prevents the peptisation.

EX: - dil. HNO_3 is added to the distilled water for washing the $AgCl_2$ solution.

Completeness of precipitation:-

To verify that all of the ion or ions precipitating have been removed, the chemist performs a completeness of precipitation test.

The chemist removes the liquid above the precipitate and adds a small amount of the precipitating agent to the liquid to determine if any more precipitate will form.

Test for completeness of Precipitation:-

Centrifuge and, without decanting the solution, add a drop of reagent so it runs down the wall of the test tube.

If precipitation is complete, no new precipitate will form when the reagent dissolves in the solution.

Effect of excess precipitant:-

For checking the completeness of precipitation we have to add precipitating agent in slight excess but sometimes this will increase the co precipitation impurities.

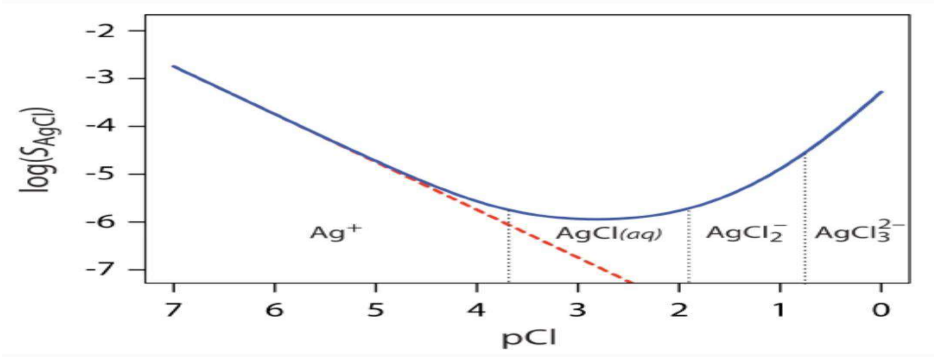
It requires that we account for every equilibrium reaction that might affect the precipitate's solubility. For example, we can determine Ag^+ gravimetrically by adding NaCl as a precipitant, forming a precipitate of AgCl.

$$Ag+ (aq) + Cl- (aq) \rightleftharpoons AgCl(s)$$

If this is the only reaction we consider, then we predict that the precipitate's solubility, S AgCl, is given by the following equation.

$$S\ AgCl = [Ag^+] = K\ sp\ [Cl^-]$$

Equation suggests that we can minimize solubility losses by adding a large excess of Cl^-. In fact, as shown in adding a large excess of Cl^- increases the precipitate's solubility.



Effect of pH on the precipitate:-

If the pH of the dissolution of the solubility of the precipitates increases with decreases the pH of the solution. At the solubility of precipitate whose anion is add from weak acid because of the acid which tends to the combines with anion of the solid.

$$MA \rightarrow M^+ + A^-$$

$$\downarrow$$

$$H$$

$$\downarrow$$

$$HA$$

Anion 'A' can combine with the proton is increases the solubility of the precipitate. Consider for examples the solubility of calcium oxalate in presence of strong and the equilibrium is, here K sp is solubility of product constant.

$$CaC_2O_4 \rightleftharpoons Ca^{+2} + C_2O4^{2-}$$

$$K\ sp = 2.6 \times 10^{-9}$$

The anions from this calcium oxalate which can react with H^+.

$$C_2O_4^{2-} + H^+ \rightleftharpoons HC_2O_4^-$$

$$K\ sp = 6.1 \times 10^{-5}$$

$$C_2O_4^{2-} \rightleftharpoons HC_2O_4^- + H^+ \rightleftharpoons H_2C_2O_4^-$$

$$K\ sp = 6.5 \times 10^{-2}$$

The formation of oxalate says dissolution (or) solubility of calcium oxalate. Then the solubility of calcium oxalate is,

$$CaC_2O_4 = [H_2C_2O_4^-] + [HC_2O_4^-] + [C_2O_4^{-2}]$$

Effect of complex formation on precipitate:-

Complexing agent complete for the metal in a precipitate just as acid convert for the anion.

A precipitate 'MA' in the dissociation to give an M^+ and A^- ions & those metal complexes if the ligand 'L' form ML^+.

$MA \rightleftharpoons M^+ A^-$

$L^+ \rightleftharpoons ML^+$

The sum of concentration of $[M^+]$ and concentration of $[ML^+]$ is represents the analytical concentration [CM]. For example is AgBr.

$$Ag\ Br \rightarrow Ag^+ Br^-$$

$$Ag\ Br \rightleftharpoons Ag^+ + Br^-$$

$$Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+$$

$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+$$

The solubility of Ag Br is equal to

$$C_M = [Ag(NH_3)_2^+] + [Ag(NH_3)^+] + [Ag^+]$$

Temperature:-

Drying and Ignition:-

The purpose of drying (heating at about 120-150^o C in an oven) is to remove the remaining moisture while the purpose of ignition in a muffle furnace at temperatures ranging from 600-1200^o C is to get a material with exactly known chemical structure so that the amount of analyte can be accurately determined.

The precipitate is converted to a more chemically stable form. For instance, calcium ion might be precipitated using oxalate ion, to produce calcium oxalate (CaC_2O_4) which is hydrophilic; therefore it is better to be heated to convert it into $CaCO_3$ or CaO.

The $CaCO_3$ formula is preferred to reduce weighing errors as mentioned in previous lectures. It is vital that the empirical formula of the weighed precipitate be known, and that the precipitate is pure; if two forms are present, the results will be inaccurate.

Purity of precipitate:-

When a precipitate Separate from the solution. It is not always pure. It may containing various amount of impurities depends up on the nature of the precipitate of the conditions employed.

Here for example when we added excess of H_2SO_4 to the [Solution containing Ba^+2, Fe^{+3}ions]. Then the main barium sulphate precipitate is contaminated with Fe $(SO_4)_3$] analyte.

The analyte having a small quantity of other ions like is Fe (III). Fe (III) forms Ferric sulphate precipitate, which is in brown colour. i.e.; $BaSO_4$ precipitate has white colour which is contaminated by ferric sulphate.

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4$$

Digestion or Aging:-

Precipitation hardening, also called age hardening or particle hardening, is a heat treatment technique used to increase the yield strength of malleable materials, including most structural alloys of aluminum, magnesium, nickel, titanium, and some steels and stainless steels.

This is the process usually carried out to stand for 12-24 hrs at room temperature) the precipitation in contact with precipitation by warming by allowing the sometimes the Liquid from which it was formed.

The purpose is to obtain the complete precipitation which can be readily filtered.

During May also the digestion the impunities trapped in some packets Escape from these places, making "the precipitation pure, digestion (or) Aging promotes the formation of crystal shape with lesser surface area Hence Co-precipitation will be less.

Agitation: -

The agitation is uniform suspension of microbial cells in homogeneous nutrient medium. Difference between natural aging & artificial

Aging:-

Natural aging occurs throughout the life of the metal alloy. Artificial aging is a process that is used to accelerate the formation of precipitates in a solution heat-treated metal alloy to a rate that is much faster than the natural aging process.

Importance of agitation:-

To increase the rate of oxygen is transfer from the air bubble to the liquid medium.

To increase the rate of oxygen and nutrients transfer from the medium to cells.

To prevent formation of clumps of cells, aggregates of mycelium.

To increase the rate then to transfer of product of metabolism is from cell to medium.

To increase the rate or efficiency of heat transfer between the medium and the cooling surfaces of the form enters.

b) Co-precipitation and post precipitation:-

Theory of adsorption of salts having an ion in common with the main precipitate:-

Adsorption- :-

In general the surface adsorption is marked for gelatinous precipitate & least for those with micro crystal con character.

EX: - When the all the chloride has been precipitated by the excess addition of as $AgNO_3$. The Ag^+ will be adsorbed on the AgCl as $AgNO_3$.

If acetate is present in the solution the adsorbed layer consists of silver acetate. It has lower solubility.

Co-precipitation of impurities with hydrous oxide can be reduced by precipitating them at as low pH as possible. If the precipitate particles are have large surface area they exit considerable adsorption.

For example in the formation of $BaSO_4$ precipitate the mono layer of $BaSO_4$ is having residual attractive forces. So the Ba^+ can attract other ions in the solutions. Hence the precipitate of $BaSO_4$ & $BaCl_2$ is formed. The ion in common with the precipitate is Ba^{+2} ions.

Similarly the sulphate ion present in the top mono layer of $BaSO_4$, it can attract the Na^+ ion which is present in the mother analyte. So the precipitate of $BaSO_4$ & $NaSO_4$ is formed. We can remove the impurities by proper washing the precipitate.

In the $BaSO_4$ Solution is around by sodium sulphate in analyte.

Definition of co precipitation:-

Co precipitation is a kind of precipitation where soluble compounds in a solution are eliminated during the course of precipitation.

There are four types of co precipitation: (1) surface adsorption, (2) mixed-crystal formation, (3) occlusion, and (4) mechanical entrapment. (1) & (2) are equilibrium processes, while (3) & (4) arise from kinetics of crystal growth.

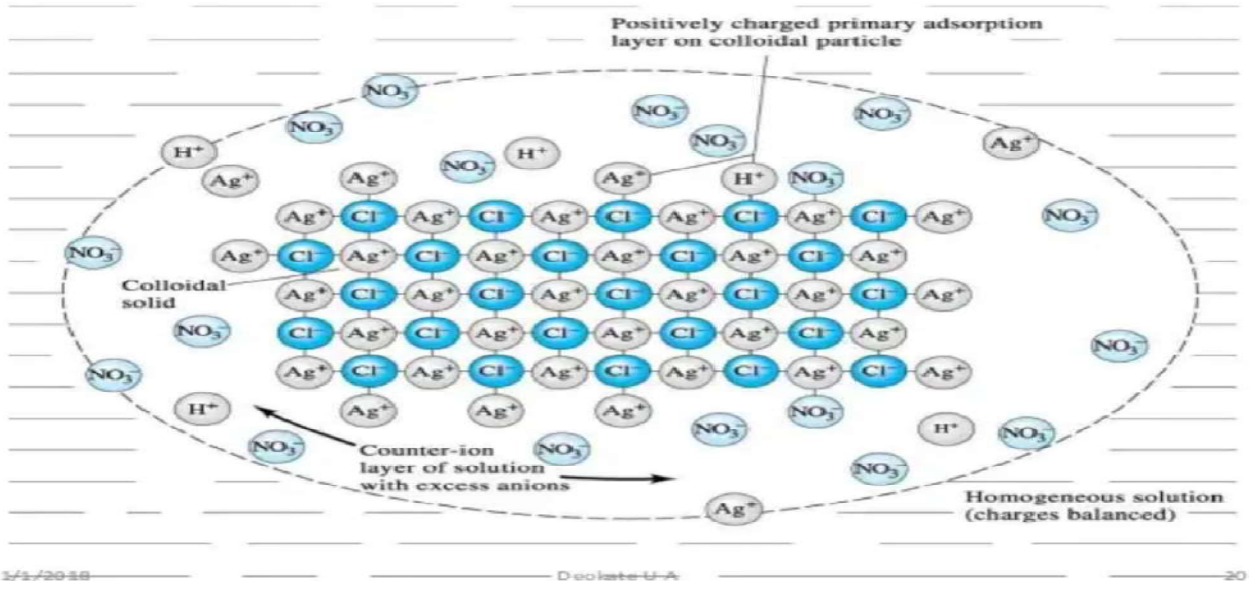
Co- precipitation in colloidal precipitates:-

This is due to sudden precipitate process the impurities are included in the main precipitate due to sudden super saturation (or) sudden precipitate formation.

The contamination of the precipitates by substances which are (Partially eliminated the precipitate of sulphate) normally soluble in the mother analyte is termed as co precipitation.

If large crystals are formed slowly` the impurities are partially eliminated. The precipitate of sulphate by this slow addition of $BaCl_2$ the sulphate is in excess of primary adsorbed ion. A positive ion says Na^+ is adsorbed as the counter ion. As more of Ba^{+2} ions are added it replaced the adsorbed Na^+ during the growth of precipitate in particles.

If the growth of the particles is fast not only Na^+ ions replaced by Ba^+, which result in the growth of the precipitate round the adsorbed Na^+.



Adsorption of solvents:-

Adsorption is a mass transfer process that is a phenomenon of adsorption of gases or solutes by solid or liquid surfaces. The adsorption on the solid surface is that the molecules or atoms on the solid surface have residual surface energy due to unbalanced forces.

Adsorption of organic substances in aqueous solution was carried out using hydrophobic silica adsorbent. Adsorbed amount was estimated using HSP (Hansen solubility parameters (HSPs) theory.

An adsorption amount estimation formula using the difference R_a of HSP values was constructed. It was suggested that affinity is an important factor in adsorption.

Adsorption is an effective methodology for the removal of organic matter.

Several studies have shown that adsorption performance is dependent on pore size, specific surface area, and the affinity between the adsorbent and adsorbed material.

In this study, we concentrated on the effect of the affinity between the surface of the adsorbent and the adsorbed matter by examining the adsorption of organic solvents from organic/aqueous mixtures using three types of hydrophobic silica adsorbents are.

Factors Affecting Adsorption:-

(i) Nature and Surface Area of the Adsorbent.

(ii) The Nature of the Adsorbed Gas.

(iii) Temperature.

(iv) Pressure of the gas.

Mixed crystal formation by occlusion and entrapment (or) Isomorphism Inclusion:-

If the impurities are the isomorphism is the precipitate it may be carried with the precipitate in the form of mixed crystals.

For example $BaSO_4$ is precipitated from a solution containing small quantity of lead ions contamination of precipitate with lead sulphate occurs through the solubility product of $PbSO_4$ is not exceeded.

This arises from the fact that both barium sulphate & $PbSO_4$ are isomorphism. The lead ions replacing sum of the Ba^+ ions throughout the crystal Lattices in a random process.

Co precipitation from the mixed crystal formation is a major factor in precipitation process. Removal of the impurities it is not achieved by simple operation like washing (or) digestion. Mixed crystal impurities are removed by recrystalization process.

Re precipitation with examples:-

In the process of returning a precipitate into a dissolved state only to precipitate it's once again.

The re precipitation method is a pure chemical technique to prepare organic nano crystals simply by injecting solution of the target compound into a poor solvent. As distilled water is usually used as poor solvent, water- soluble solvent such as alcohol, acetone was selected as the injected solution.

Definition of post precipitation:-

Post precipitation is a kind of precipitation where the precipitation of the undesirable compound occurs after the formation of the precipitate of the desired compound.

Post-precipitation can be minimized by –

Complex formation, change in oxidation state, rapid filtration of precipitate, concentration of impurities.

Post precipitation:-

Theory of post precipitation & examples of post precipitation:-

The incorporation impurities in to a precipitate after the formation of primary precipitate are known as post-precipitation.

When the solution contains two ions are one of which is rapidly & other is slowly precipitated by the same reactant.

The first precipitate is usually contaminated by the second one this process is known as post-precipitation.

These phenomenon occur with sparingly soluble substances which forms super saturated solution.

Ex: - In the precipitation of calcium oxalate in presence of magnesium, a small amount of magnesium also co precipitated as oxalate. It is digested in the mother analyte without separation. Then it appeared as insoluble precipitate which cannot be separated by washing the precipitate.

The post precipitated impurities are not soluble in water it can't removed by washing But they' are removed by re precipitation process. After then dissolving is suitable solvent.

This phenomenon is extreme is important in the separation in the metal. This is necessary standardize the experimental conditions. Then these precipitations of metal to avoid the contamination from other metal ions through co precipitation.

A complexing ion is usually added that will permit the precipitation of a metal ion by a precipitating agent & prevent precipitation of a second metal ion present in the mixture.

The addition of tartarate (present) prevents the precipitate of hydrous ferric oxide at the slightly alkaline conditions needed for precipitation of nickel with di methyl glyoxime.

Such reagents are masking agents, some masking agent used for various metal ions.

S.NO	Element	Masking agents
1	Ag	Br^-, Cl^-, CN^-,I^-, NH_3^-,SCN^-
2	Al	Acetate, Citrate, $C_2O_4^{2-}$, EDTA, OH^-, F^-, Sulpho salicylic acid
3	Ba	[APCA] Amino poly carboxylic acid, Tartarate
4	Br	Phenol for Br_2
5	Ca	APCA, Citrate, Tartarate, Poly phosphate
6	Cd	APCA, Citrate, CN^-, SCN^-, $S_2O_3^{2-}$
7	CN^-	HCHO, Hg^{2+}
8	Co	APCA, Citrate, CN^-, Tartarate
9	Cr	APCA, Citrate, tartarate, NaOH
10	Cu	APCA, Citrate, CN-, Tartarate
11	Fe	APCA, Citrate, CN^-, Tartarate,SCN^-,PO_4^{3-}
12	Hg	APCA, Citrate, CN^-, Tartarate
13	Ni	APCA, Citrate, CN^-, Tartarate

14	Pb	APCA, Acetate, Tartarate
15	Pt	APCA, Acetate, Tartarate
16	Pd	APCA, Acetate, Tartarate
17	Mo	APCA, Acetate, Tartarate
18	Mn	APCA, Acetate, Tartarate

Difference between co precipitation and post precipitation:-

S.NO	Co precipitation	Post precipitation
Definition	It is a type of precipitation where soluble compounds in a solution are removed during the course of precipitation.	It is a type of precipitation where the precipitation an undesirable compound occurs after the formation of the precipitate of the desirable compound.
Degree of contamination	High	Low
Time of precipitation	During the desirable precipitation	After the desirable precipitation
Examples	Precipitation of silver ions with other ions during the silver chloride precipitation.	Formation of calcium oxalate after the precipitation of magnesium oxalate.

Conditions for obtaining pure and quantitative precipitates:-

The Precipitation for Solution if super saturation is low Possible leads to the formation of large particles free from contamination. Here purposes in the use of a very dilute solution. The precipitate should be carried out the dilute solution. This will helps in super Saturation.

Super saturation = Q-S

Relative super saturation = Q-S / S

The reagent should be mixed slowly with constant stirring this will reduce the degree of super saturation. The slow drop addition a slight excess of reagent is used for complete precipitation.

The precipitate is carried out in hot conditions either one regent (or) both - precipitating agent & Sample solution can be heated. Then the heating temperature is boiling point of solvent.

For washing the precipitate the dilute electrolyte solutions are used.

The obtained crystalline precipitate is digesting on water both preferably over night; this will minimize the co precipitated impurities.

In case of should not be any post precipitation impurities on the main precipitate.

In case of entrapped (or) other type of impurities the precipitate is dissolved & re precipitate is carried out for getting pure precipitate.

The precipitation from homogeneous solution is generally employed for decreasing super saturation. In this the reagent is produced in the solution by homogeneous reaction, these are called PEHS Method.

The advantage of PFHS method is we get pure & big crystals.

c) Precipitation titrations:-

Precipitation is a technique used to separate a mixture based on the solubility of its components. The solubility of a compound depends on the ionic strength of the solution, its pH, and temperature. A dissolved compound can be precipitated out of solution by introducing a counter ion.

Precipitation titration is a type of titration which involves the formation of precipitate during the titration technique. In precipitation titration, the titrant reacts with analyte and forms an insoluble substance called precipitate. It continues till the last amount of analyte is consumed.

Principle:-

In precipitation titrations the formation of precipitates is used as the basis of the titration. The point at which as stoichiometric amount of the titrant is added to precipitate completely the ion to be estimated presented in a given volume of the solution is the end point.

Example: – To determine the concentration of chloride ion in a certain solution we can titrate is this solution with silver nitrate solution (whose concentration is known).

The chemical reaction occurs as follows:

$$Ag^{+}+Cl^{-}\rightarrow AgCl$$

The quantitative determination of analyte by forming a precipitate by using precipitating reagent is called precipitation reagent. Titration is a process by which the conc. of unknown substance in solution is determined by adding measured amount of standard solution. That's a react with the unknown. Then the cone of unknown can be calculating by using stoichiometry of the reaction & the number of moles of standard solution need to reach by end point.

Indicators for precipitation titrations:-

There are several examples of an indicator forming a coloured compound with a titrant.

The most method for determine chloride as an example. The chloride is titrated with standard $AgNO_3$ solution, a soluble chromate salt is added as the indicator.

These produce a yellow solution when the precipitate of chloride is completed. The First excess of Ag^{+} reacts with indicator to precipitate red silver chromate.

$$Cl^{-} + AgNO_3+K_2CrO_4\rightarrow AgCl$$

$$2Ag^{+} +K_2CrO_4\rightarrow Ag_2CrO_4$$

Determination of halides:-

Determination of halides by using Mohr's method:-

In 1856 Mohr introduced it.

In the determination of halides by using Mohr's method adding the $AgNO_3$ Solution to the sample to maintain the neutral medium.

We can increase the acidic medium in the titration then chromate ions the indicator present in the solution is converted into per chromate. It is acts as weak acid in the solution.

$$H^+ + CrO_4^{2-} \rightarrow HCrO_4^{2-}$$

Due to the formation of per chromate in the solution more Ag^+ ions are required to formation of silver chromate (Ag_2CrO_4) in the solution to the end point.

If the basic medium increases in the solution then the hydroxide ions are reacted with Ag^+ ions it gives $(AgOH)_2$.

$$Ag^+ + 2OH^- \rightarrow (AgOH)_2$$

Iodide can't be determined by using Mohr's method because silver iodide can absorb strongly chromate ions.

Adsorption indicators:-

The indicator reaction takes place on the surface of precipitate. The indicator which is a dye, exist in a solution as the ionized form usually an anion. Consider the titration of chloride with Ag^+ before the equivalence point, Chloride ion is in excess and the primary absorbed layer is Cl^-. This repulses the indicator anion & the more loosely held Secondary layer of absorbed ion is cations. Such as Na^+

$$AgCl: Cl^-: Na^+$$

Beyond the equivalence point Ag^+ is an excess and the surface of the precipitate becomes positively changed. If the replacing of Na^+ ions by the Ag^+ ions. This will now attract indicator anion.

$$AgCl: Ag^+: ion^-$$

The colour of indicator is different from that of the can absorbed indicator. The degree adsorption of the indicator can be decreased by increasing the acidity.

Examples of adsorption indicators:-

Indicator	Use	Colour change at end point	Experimental conditions
Fluorescence	Cl^-, Br^-, I^- with Ag^+	Yellow green- pink	Neutral or weakly basic
Di chloro Fluorescence	Cl^-, Br^- with Ag^+	Yellow green-red	pH range 4.2-7
Tetra bromo Fluorescence	Br^-, I^- with Ag^+	Pink- red violet	Ethanoic acidic medium
Methyl Violet	Cl^- with Ag^+	-	Neutral medium
Bromo Phenol blue	Cl^- with Ag^+	-	Faintly acidic medium
Ortho Chromo-T	Chromate with Pb^{+2}	-	Neutral medium

Precautions:-

In this method, neutral medium should be used since, in alkaline solutions, silver will react with the hydroxide ions forming AgOH. In acidic solutions, chromate will be converted to dichromate. Therefore, the pH of solution should be kept at about 7. There is always some error in this method because a dilute chromate solution is used due to the intense color of the indicator. This will require additional amount of Ag^+ for the Ag_2CrO to form.

Limitations:-

Allowable pH range is 6.5 to 10. Below pH 6.5 there is increased in solubility of silver chromate. Above pH 10 the end point comes too late and silver hydroxide is also precipitated. If the solution is alkaline make it acidic with nitric acid then neutralize it by adding sodium bi carbonate or borax. If appreciable amount of Ammonium salts are present the pH should not exceed7.2. In reverse titration iodides and bromides cannot be titrated.

Determination of halides by using Volhard's method:-

In 1874 Volhard's designed the method of estimation of silver ions [$AgNO_3$] in dilute acid solutions by titrating against a standard thio cyanide solution in the presence of ferric salt [Ferric ammonium sulphate] as indicator.

It has been extended to estimate chloride, bromide and other several analyses.

$$AgNO_3 + NH_4SCN \rightarrow AgSCN + NH_4NO_3$$

Principle:-

Halides can be determined by the excess addition of $AgNO_3$ solution to the sample. The untreated $AgNO_3$ is titrated with standard ammonium thio cyanide using Ferric alum as an indicator.

$$Cl^-, I^-, Br^- + \text{excess } AgNO_3 \rightarrow AgCl, AgBr, AgI + NH_4NO_3$$

$$\text{Untreated } AgNO_3 + (NH_4)_2\,SCN + \text{Ferric AgSCN} \rightarrow [AgSCN] + NH_4NO_3$$

$$[Fe\,(NH_4)\,(SO_4)]^{+3} + NH_4SCN \rightarrow [Fe\,(SCN)^{+2}] + 2(NH_4)2SO_4$$

$$Fe^{3+} + SCN^- \rightarrow Fe\,(SCN)^{2+}$$

Preparation of Solutions:-

Preparation of 0.01 N $AgNO_3^-$ solutions:-

Accurately weighted 0.42 - 4.6g of $AgNO_3$ is taken in to a 250ml volumetric flask. It is dissolved in distilled water & make up to the mark with 250mL volumetric flask.

Preparation of ferric alum indicator:-

Dissolve 4g of Ferric alum in l0mL of IN HNO_3 boil the solution to remove oxides of nitrogen cool & dilute with 30mL of distilled water.

Preparation of Ammonium thio cyanide:-

Accurately weighed sufficient amount of ammonium thio cyanide is a taken in to a 250ml volumetric flask. Then it is dissolved in distilled water & make up to the mark.

Procedure:-

To take 1(or) 2g of sample dissolved in l00mL of benzene solution for this 10mL of solution taken & then added 45mL of $AgNO_3$ Solution. Shake the solution for 5 min. Then to this added a hydrous methanol, stand this solution for 10-15 min. The untreated $AgNO_3$ is titrated with standard ammonium thio cyanide by using ferric alum as an indicator.

Determination of halides by using Fajans Method: - (Adsorption Indicator):-

In 1923-24 Fajan's introduced the method. It is used as an adsorption indicator.

The action of these indicators are based on the simple fact that the endpoint the indicators get adsorbed by the precipitate AgCl and during the process of adsorption, a change in colour of the indicator will takes place which may result in a substance of different colour.

The Fajan's method uses an adsorption indicator, an organic compound that adsorbs onto or desorbs from the surface of the solid in a precipitation titration,

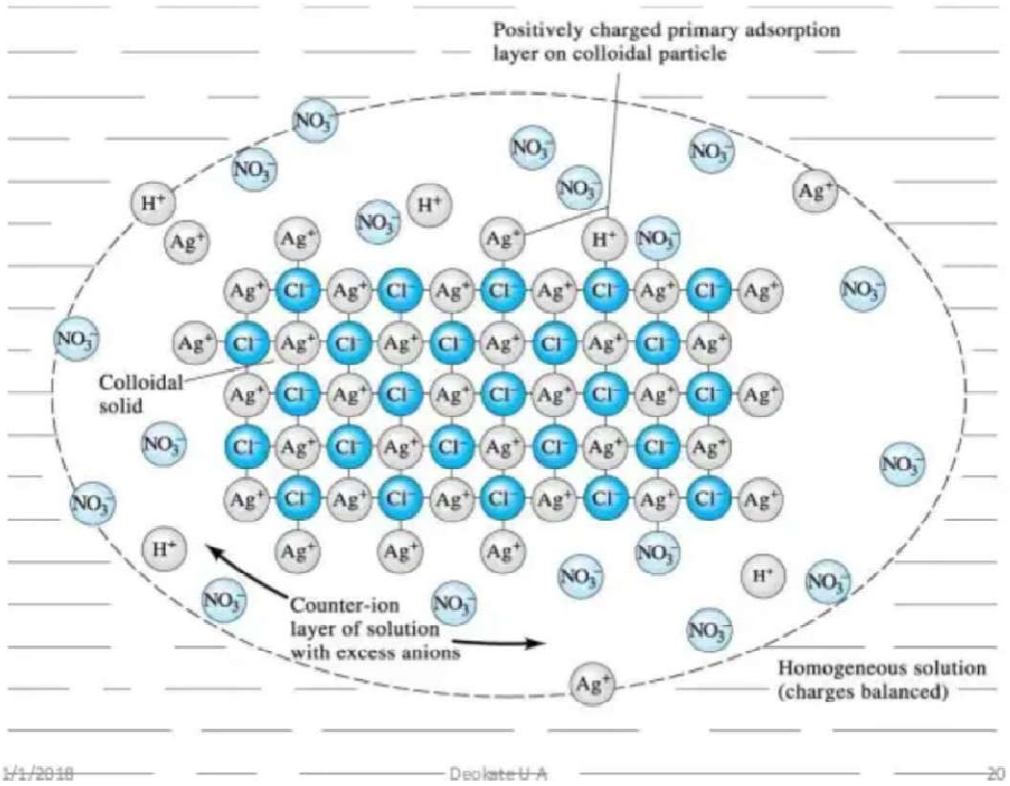
The adsorption or desorption occurs near the equivalence point and results not only in a color change but also in the transfer of color from the solution to the solid or vice versa.

Fluoresce in is a typical adsorption indicator useful for the titration of chloride ion with silver nitrate.

In the aqueous solution, fluoresce in is partially ionized to hydronium ions and yellowish green colored negatively charged fluorescent ions. The fluorescent ion forms a dark red silver salt.

Before the equivalence point, Cl^- is in excess, and the primary adsorbed layer is Cl^-.

This repels the indicator anion, & the more loosely held secondary (counter) layer of adsorbed ions is cations, such as Na^+.



Beyond the equivalence point, Ag^+ is in excess, and the surface of the precipitate becomes positively charged, with the primary layer being Ag^+. This will now attract the indicator anion and adsorb it in the counter layer.

Titrations involving adsorption indicators are rapid, accurate, and reliable, but their application is limited to the few precipitation titrations that form colloidal precipitates rapidly.

Procedure:-

To take the Cl^- sample and then to this added 30ml of purified distilled water and then to this added 3 drops of 5% of CrO_4^{2-} solution as a indicator, then these solution is titrated with 0.5m $AgNO_3^-$ solution. Then yellow colour solution is formed. Until orange colour of Ag_2CrO_4 precipitate is a formed.

Fajan's method:-

Advantage: - capability for different pH range and selectively with different indicator.

Disadvantage: - Difficulty with dilute solution should not be a high background ionic level

Limitations of Precipitation Titration:-

A few numbers of ions such as halide ions (Cl^-, Br^-, 1^-) can be titrated by precipitation method.

Co-precipitation may be occurred.

It is very difficult to detect the end point.

Precautions:-

The AgCl should not be allowed to coagulate into large particles at the equivalent point since this will greatly decrease the surface available for adsorption of the indicator.

A protective colloid such as dextrin should be added to keep the precipitate highly dispersed .in the presence of dextrin the color change is reversible and if the end point is overrun, one can back titrate with a standard chloride solution.

The adsorption of indicator should start just before the equivalent point and increase rapidly at the equivalent point.

Some unsuitable indicators are so strongly adsorbed that they actually displace the primary adsorbed ion well before the equivalent point is reached.

The pH of the titration medium must be controlled to ensure a sufficient concentration of the ion of the weak acid or base indicator.

Fluoresce in for e.g., has a (Ka = 10 – 7) and in solutions more than acidic than pH 7 the concentration of Fluoresce in ions is so small that no color change is observed.

Fluoresce ion can be used only in the pH range of about 7 to 10. It is preferable that the indicator ion be opposite in charge to the ion added as the titrant adsorption of the indicator will then not occur until excess titrant is present.

UNIT-II

PRECIPITATION METHODS-II

Precipitation from Homogeneous Solution (PFHS):-

Precipitation from homogeneous solution is a technique in which a precipitating agent is generated in a solution of the analyte by a slow chemical reaction. Local reagent excesses do not occur because the precipitating agent appears gradually and homogeneously throughout the solution and reacts immediately with the analyte. As a result, the relative super saturation is kept low during the entire precipitation.

In general, homogeneously formed precipitates, both colloidal and crystalline, are better suited for analysis than a solid formed by direct addition of a precipitating reagent.

Theory of PFHS:-

Here the precipitation from solutions in which super saturation are low possible leads to the formation of precipitations of large particles free from contamination.

For this purpose the use of dilute solution & their slow drop wise addition (To avoid local excess of the reagents are advised). But they particle limitations like solubility uses in dilute solutions & long periods of time required for the precipitation process.

Further it is not possible to eliminate excess local super saturation even with the most efficient stirring of the solution.

Precipitation from homogeneous solution is a technique which in many cases can get over the problems.

In PFHS the reagent & the solute are mixed & that conditions where a precipitate can't form. Then the conditions are altered slowly in a uniform manner throughout the solutions until they allow the precipitation takes place. This procedure avoids local excess of the reagent concentration thus facilitating the formation of pure crystal of the precipitate. Throughout their slow grow entire solutions.

A well known example of PFHS involves use of 'urea' to generate hydroxide ions for the precipitation of hydroxides of aluminum, iron, and other heavy metal ions. The precipitating hydroxide ions generated by the following reaction.

$$NH_2\text{-}C{=}O\text{-}NH_2 + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$$

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3$$

Methods of PFHS:-

1. Change in pH:-

a) Increase in pH:-

Here precipitation of aluminum as $Al(OH)_3$ by using urea hydrolysis method in which the reagent of OH^- ion is generated uniformly throughout the solution.

Here we use controlled increasing of pH as conditions for the precipitation process.

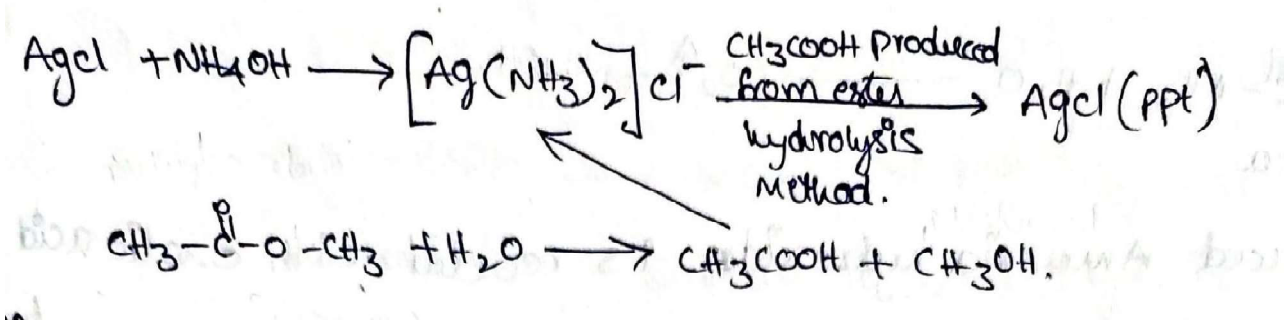
$$NH_2\text{-}C{=}O\text{-}NH_2 + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$$

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3$$

Al, Si precipitations are prepared by PFHS is most use full for the chromatographic purpose & as a cation exchanges. The crystals obtained by PFHS are also used for crystal studies.

b) Decreases in pH:-

AgCl & AgBr precipitation by PFHS methods utilizes the decreasing pH. For this first we add NH_4OH, it like act if it more causes neutralization of acid produced by ester hydrolysis. Then causes decreasing the pH, which is constant to our experiment. Then we get [Ag $(NH_3)_2$] C1 silver ammonium complex. It is soluble in nature. Then we add ester to this complex & maintained of controlled pH of the solution. The produced acetic acid (CH_3COOH) neutralize the ammonia, Finally AgCl precipitate is formed.



2. Ion releases:–

I) Anion released:-

Aluminum ion is precipitated as Al (OH) $_3$. This method is always similar with the urea hydrolysis in which the precipitating agent. i.e.; anion release slowly we can solution obtained by the controlled hydrolysis of suitable compounds under conditions necessary for the formation of Insoluble precipitate.

Barium precipitated as barium sulphate:-

In this first we add diethyl sulphate to the barium chloride solution under the hydrolysis of diethyl sulphate. Then the sulphate ions are generated homogeneously throughout the solution, finally we get a $BaSO_4$ precipitate.

$$BaCl_2 + (C_2H_5)_2SO_4 + H_2SO_4 \rightarrow BaSO_4$$

Calcium oxalate preparation:-

Here the oxalate ions are released by di methyl oxalate. We mix the reagent di methyl oxalate & urea to the sample solution $CaCl_2$. Under hydrolysis of di methyl oxalate it gives oxalic acid and methanol.

$$CaCl_2 + (CH_3)_2\,C_2O_4 + 2H_2O \rightarrow COOH\text{-}COOH + 2CH_3OH$$

Under the hydrolysis of urea it gives NH_4OH.

$$NH_2\text{-}C{=}O\text{-}NH_2 + H_2O \rightarrow CO2\uparrow + NH_4OH$$

The produced ammonia hydroxide is reacted with oxalic acid, it gives ammonium oxalate. The produced oxalate ions are generated homogeneously throughout the solution; finally calcium oxalate precipitate is formed.

$$COOH\text{-}COOH + NH_4OH \rightarrow (NH_4)_2C_2O_4\ (NH_4)^{2+} + C_2O_4^-$$

$$Ca^{+2} + C_2O_4^- \rightarrow CaC_2O4$$

II) Cation released:-

Cation released at constant pH:-

It can be achieved by slowly destroying a soluble complex. For example the ligand EDTA destroyed CO_2 & H_2O by boil with H_2O_2 it can be following as.

$$EDTA+H_2O_2 \rightarrow CO_2+H_2O$$

Metal EDTA complex treated with H_2O_2 in which situations metal ions are slowly generated in the solution by the decomposition of EDTA as CO_2 & H_2O.

$$M\text{-}EDTA+H_2O_2 \rightarrow CO_2+H_2O+M^{+}$$

$$Ba\text{-}EDTA+H2O_2\Delta \rightarrow CO_2+H_2O+Ba^{+2}$$

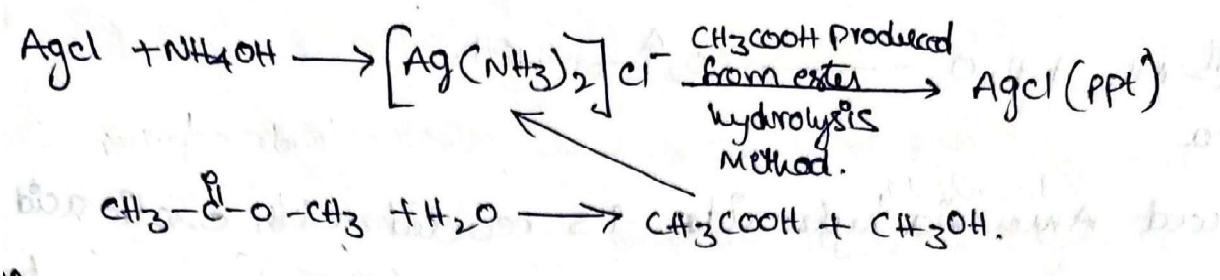
$$Ni\text{-}EDTA \rightarrow CO_2+H_2O+Ni^{+2}$$

In the determination of suphate ions, Ba-EDTA is added to the sample solution of SO_4^{2-} ions. In which the situation of Ba^{+2} ions are slowly generated in the solution by the decomposition of EDTA as $CO_2 + H_2O$. Finally we get a $BaSO_4$ precipitate.

$$Ba^{+2}+SO_4^{-2} \rightarrow BaSO_4$$

Cation released at pH decreases:-

AgCl & AgBr precipitation by PFHS methods utilizes the decreasing pH. For this first we add NH_4OH, it like act if it more causes neutralization of acid produced by ester hydrolysis. The decreasing pH in which is constant to our experiment. Then we get [Ag $(NH_3)_2$] C1 silver ammonium complex. It is soluble nature. Then we add ester to this complex & maintained of controlled pH of the solution. Then we get an acetic acid (CH_3COOH).



Cations are released by the addition of other cations:-

A soluble solution of cations is added to the metal chelating complexes. The cations are released throughout the solution by the replacement of cations from metal chilling complexes.

$$Ni^{+2}+ Ba\text{-}EDTA \rightarrow Ni\text{-}EDTA + Ba^{+2}$$

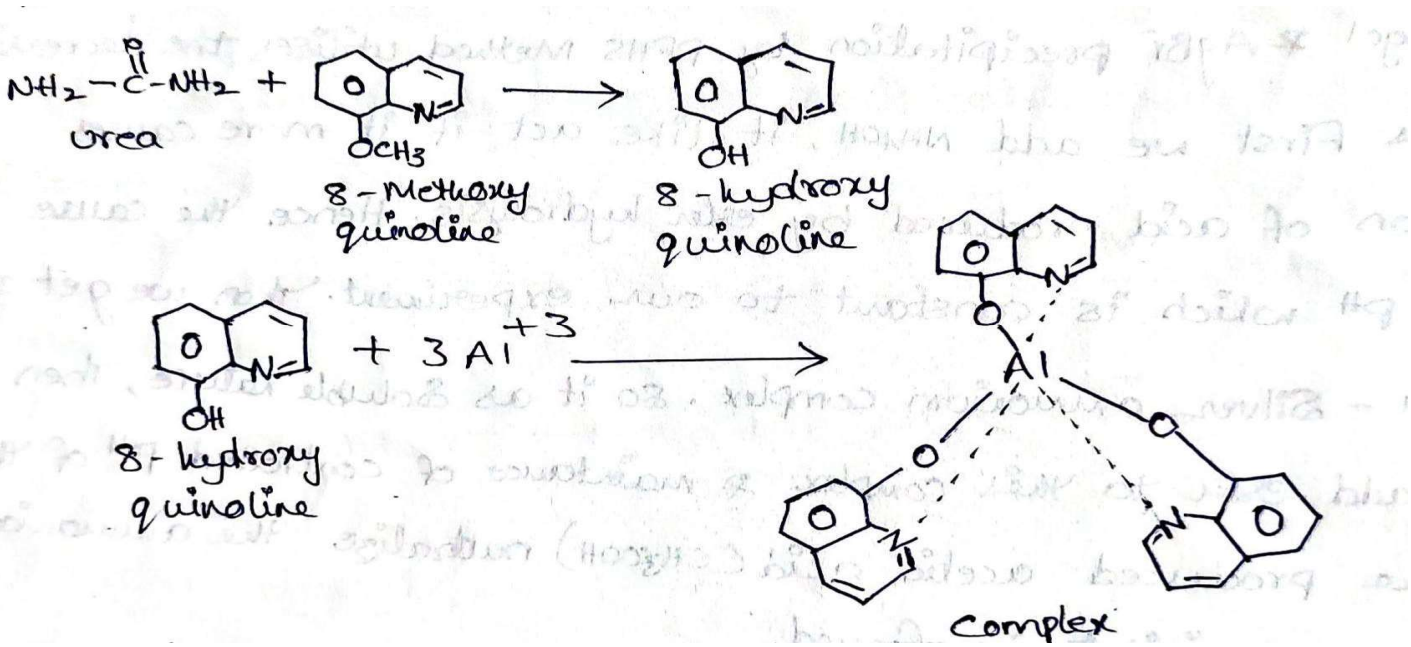
The Ni-EDTA complexes are more stable then Ba-EDTA complex. Ba^{+2} replace by the Ni^{+2} ions. That means Ba^{+2} ions are generated homogeneously throughout the solution.

3. Reagent Synthesis:-

Aluminum (or) Nickel these are precipitated as complexes form.

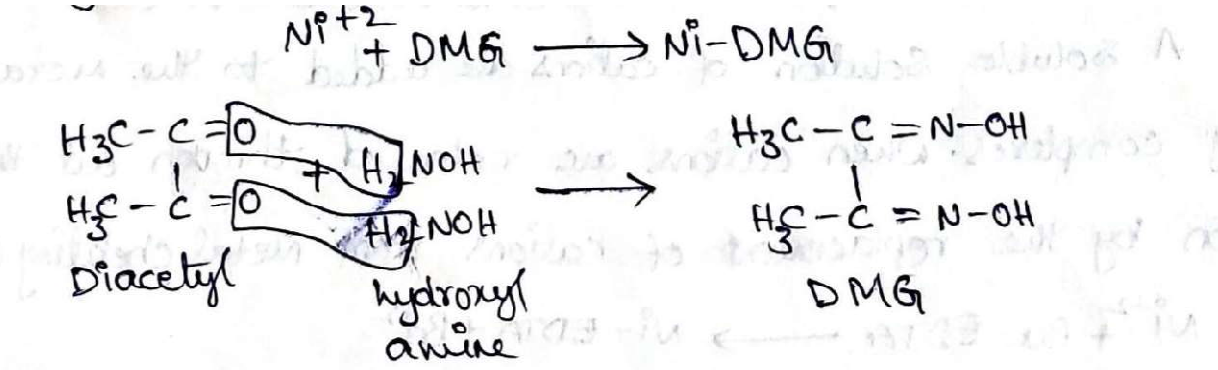
Determination of Alumina:-

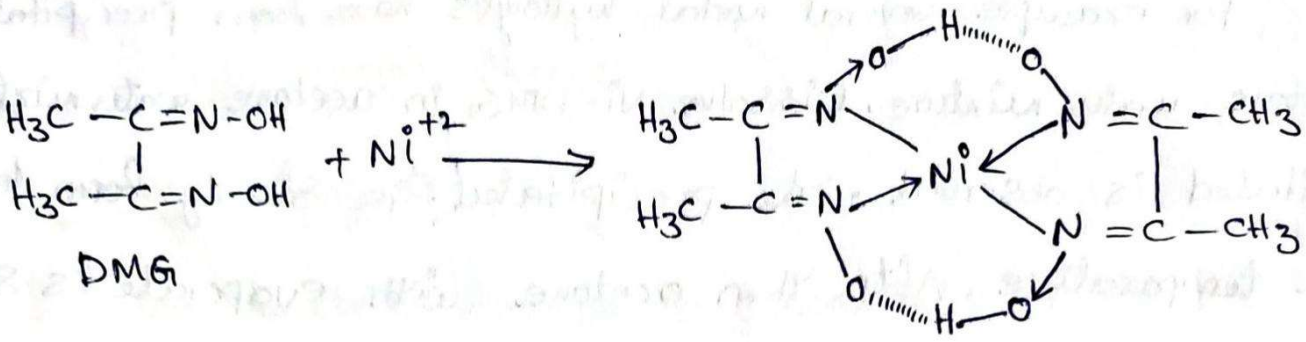
The Aluminum forms complex with 8-hydroxy quinoline. In this situation 8-hydroxy quinoline is prepared by the urea & 8-methoxy quinoline.



Determination of Nickel:-

Nickel forms complex with di methyl glyoxime. In which situation di methyl glyoxime is prepared by the addition of di acetyl and hydroxylamine.





4. Change in oxidation state (or) Redox systems:-

Cerium (IV) is prepared as $Ce(IO_3)_3$ by adding of potassium iodide & bromated. Here Cerium (III) slowly oxidized homogeneously throughout the solution. This process is used for separation of cerium from another rare earth metals. The reaction between cerium & bromated is very slow.

$$Ce(IO_3)_3 + BrO_3 + KIO_3 \rightarrow Ce(IO)_4$$

5. Photo chemical reactions or reduction:-

Per iodate is converted in to iodate. The produced iodate is generated homogeneously throughout this solution by using this method cerium & thorium can be converted into precipitate form.

$$IO_4^- + \text{Sunlight} \rightarrow .IO_3^-$$

6. Precipitation from mixed solvents:-

This is nothing but recrystalization process. Generally metal chelating complexes are insoluble in water. These are soluble in organic solvents. These are a solution of all the reagent is prepared by using solvent water mixture. The solvent should be more water then when the solvent is slowly evaporated, the metal-chelate is precipitated under homogeneous conditions.

For example several metal hydrolysis have been precipitated from an acetone with mixture. The dissolved Ni- DMG is acetone - water mixture. No precipitated is observed. The precipitated is slowly form let the p higher temperature. After then acetone with evaporate is slowly. Finally precipitate is formed. In this method selectivity of suitable Solvent is importance.

S.NO	Metal ion	Reagent	Precipitate form
1	Al, Fe^{+3}, Ga	Urea	Hydroxide
2	Sn^{+4}, Zr	Acetamide	Hydroxide
3	Zr, Mg	Tri ethyl phosphate and urea	Phosphate
4	Ba, Ca, Sr, Pb	Di methyl sulphate	Sulphate
5	Pb, Sb, Bi, Mo, Cu, Ag, Cd	Thio acetamide	Sulphide
6	Fe (III), Th	Per iodate, 2-hydroxy-ethyl acetate	Iodate
7	Ba, Al	Urea, 8-hydroxy quinoline	8-hydroxy quinoline complex
8	Ni	DMG	DMG-complex

Applications:-

b) Gravimetric determinations:-

Nature of species:-

The chemical species are specific forms of a particular element in terms of isotopic composition, electronic (or) oxidation state, and complex (or) molecular structure. If one atom is identical to another, we can say they are the same chemical species.

A chemical species is a chemical substance (or) composed of chemically identical molecular entities that can explore the same set of molecular energy levels on a characteristic of the time scale.

The species can be atom, molecule, ion, radical, and it has a chemical name and chemical formula.

It is introduced the purpose of statement of physical appearance.

Preparation of the solutions:-

This may involve several steps including adjustment of the pH of the solution in order for the precipitate to occur quantitatively and get a precipitate of desired properties, removing interferences, adjusting the volume of the sample to suit the amount of precipitating agent to be added. Gravimetric analysis usually involves precipitation of analyte from solution.

1st step is – Sampling; Representative of bulk.

2nd step – Prepare the analyte solution (Dissolution) may need.

Here the preliminary separation to separate potential interferences before precipitating analyte adjustment of solution condition (pH/temp/volt/conc. of test substance) to maintain low solubility of precipitate & max precipitate formation. **E.g.:-** Calcium oxalate insoluble in basic medium.

Most of the substances are readily solute in water and can be used as such, some required special treatment as treatment with HCI, HNO_3, or fusing with basic flux.

Limitations:-

The chief disadvantage of this method is that it is very time-consuming. The chemist in today's world prefers other methods over this method. The gravimetric analysis, in general, can provide analysis of a single element, or a limited group of elements, at a time.

Interferences:-

Interference is a substance, other than the assayed material, that can be measured by the chosen analytical method or that can prevent the assayed material from being measured. Interferences cause erroneous analytical results.

Impurities in a sample may interfere with the analysis of the substance of primary interest. Thus, in the analysis of trace concentrations of metals in rivers, organic substances can cause erroneous results. These interferences must be removed prior to the analysis.

Applications:-

Extensive numbers of inorganic ions are determined with excellent precision and accuracy. Routine assays of metallurgical sample. Here relative precision of 0.1 to 1%. Good accuracy

Disadvantages:-

Here careful and time coglasswar, scrupulously clean glassware. Here very accurate weighing, co precipitation.

Inorganic precipitants:-

Inorganic reagents:-

Gravimetric analysis is concerned with the process of producing & weighing of compound (or) element in as pure for possible. After some form of chemical treatment has being carried out the substance to be examine.

Traditional gravimetric determinations have been concerned with the transformation of an element, ion (or) radical to be determined in a pure stable compound. Which is suitable for direct weighing are for that are for conversion into another chemical form can be readily quantified.

The mass of the element to original substance can readily calculate from knowledge of the formula of the compound and relative masses of the constant element.

Inorganic precipitating agents:-

The majority of inorganic precipitates function by forming sparingly soluble salts with metal ions. Most of the reagents are relative informing the insoluble salts under specified conditions.

These are used only for specific purpose b/w the reagents are mostly present in all conditions. So co precipitation and post precipitate increases.

Then inorganic precipitates are used for the determination of inorganic ions.

1. Determination of chloride:-

The aqueous solution of chloride is acidified with dil. HNO_3. Here in order to prevent the precipitation of the other salts & such as phosphate and carbonate.

A slight excess of Ag is precipitated as AgCl. Here to prevent the formation of silver with other ions of (dil HNO_3). The formed residue is dried at 130-150°c finally weighed as AgCl.

AgCl is worked with dil. HNO_3. Ag Cl is light sensitive compound; it can be decompose into Ag^+ & Cl^- in presence of light.

The decomposition is minimizing by covering the beaker are funnel carrying AgCl with black paper. The melting point of AgCl is 455°c.

Procedure: –

Accurately weighed out 0.2g of solid sample of chlorine is taken. It contains 0.1g of chlorine. It is transferred in 250mL conical flask. Then to this added 0.5mL of dil. HNO_3 & add drop by addition of 0.5M conc. $AgNO_3$ solution to the chlorine solution. Ag^+ as precipitated AgCl. The formed precipitate is washed with dil. HNO_3. Which taken in to a crucible. It is ignited. After then it is dried and weighed as AgCl. The temperature is 130-150°c. Finally, to determined the chlorine in inorganic precipitants.

2. Determination of sulphates:-

Principle:-

The measure consists in slowly by adding of dilute solution of $BaCl_2$ to a hot solution of sulphate slightly addicted with HCl.

$$Ba^{+2} + SO_4^{2-} + HCl \rightarrow BaSO_4$$

Then it is filtered and precipitate is washed with H_2O, carefully ignited and weighed at $BaSO_4$. It carried about we readily acid solutions in ordered to prevent the Ba salts of anions, such as chromate, carbonate & phosphate.

Procedure:-

Accurately weighed out about 0.3g of solid contains 0.05 - 0.06g of sulphur. It is transferred in to a beaker (or) conical flask. Then to this added 25mL of distilled water and add 0.7mL of dil. HCl & heat the solution. Then it is titrated with 5% $BaCl_2$ (drop wise addition of $BaCl_2$ from the burette). Then we get a $BaSO_4$ Precipitate. The formed precipitate is washed with dil. HCl and then taken in to a crucible. After then it is ignited and dried and weighed as a $BaSO_4$ precipitate.

Organic precipitate reagents:–

A variety of organic reagents are available for almost cell of inorganic ions. These reagents are used not only precipitation and also used for the solvent extraction.

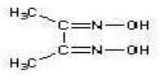
For various metal ions the precipitation with their reagents results in the formation of sparingly soluble non ionic compounds (or) complexes, since they are covalent compounds. Hence they are in soluble in aqueous medium and soluble in organic solvents. Organic precipitates are preferred inorganic precipitates. If the metal ions are very low concentration precipitation of these ions with inorganic precipitates gives very low weight precipitates.

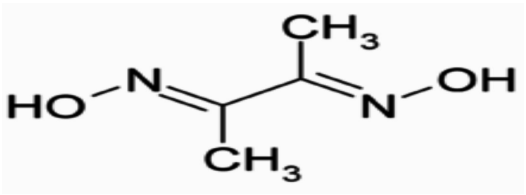
In the situation we get more errors. The getting's low errors. The quality of precipitate being weighed should be high as possible. Another type of advantage is due to ionic nature of inorganic precipitates causes adsorption other ions in its surface. But organic precipitates form mostly covalent precipitates.

Co precipitates & post precipitated impurities are not observed. Controlled of pH and also masking agents are used. These are most stable when compared to inorganic which are change to other forms, by the ignition of precipitate.

1. Di methyl glyoxime:-

Structure:-





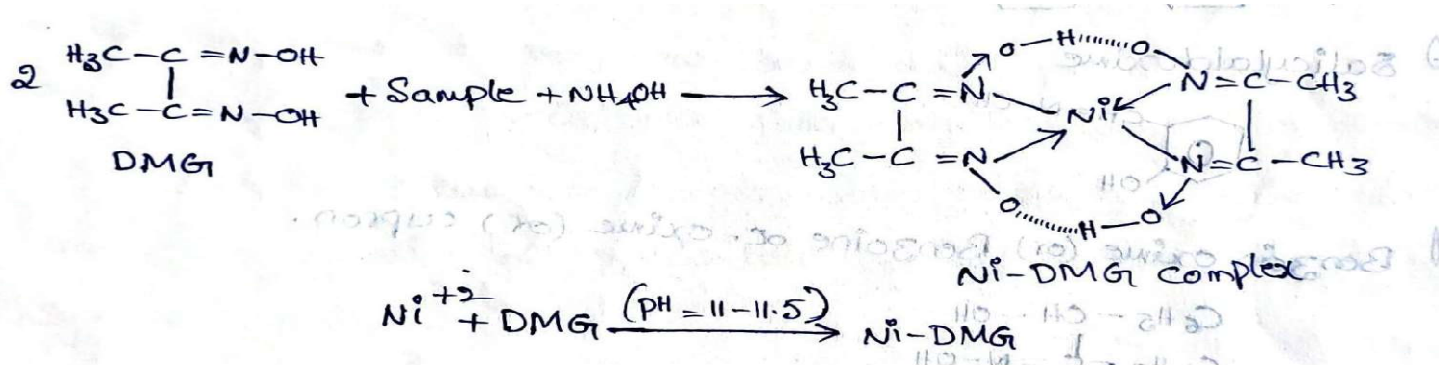
Preparation of reagent: -

It is slightly soluble in water. To take 0.4g of di methyl glyoxime is dissolved in 1% ethyl alcohol. The DMG is soluble in ethyl alcohol, acetone, Ether. It is insoluble in water. The Ni^{+2} form a complex with DMG in presence of NH_2OH. Solution of leads salts gives a yellow precipitates with DMG.

Procedure:-

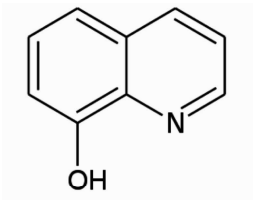
To take analyte of acetic acid solution Ni^{+2}, then added of required quantity of DMG in slide excess pH of the solution is slowly increased by the addition of NH_4OH to sample with constant stirring, the temperature is 100-120°C

Factor: - Ni-DMG contains 20-32% of Ni



2. Oxine (or) 8-hydroxy quinoline:-

Structure:-



8-hydroxy quinoline (or) oxine is almost colorless crystalline solid. The melting point of oxine is 45-74°C & also insoluble in water & soluble in ether and acetone.

Preparation:-

2g of oxine dissolved in 100mL 2N acetic acid.

Procedure:-

Precipitation of formed ions can be dried at suitable temperature and weighed as complexing form.

$$\text{Sample} + NH_4OH + \text{oxine} \rightarrow \text{Precipitate}$$

The conversation takes place in alkali medium by the addition of urea (or) ammonium hydroxide in drop wise with constant stirring.

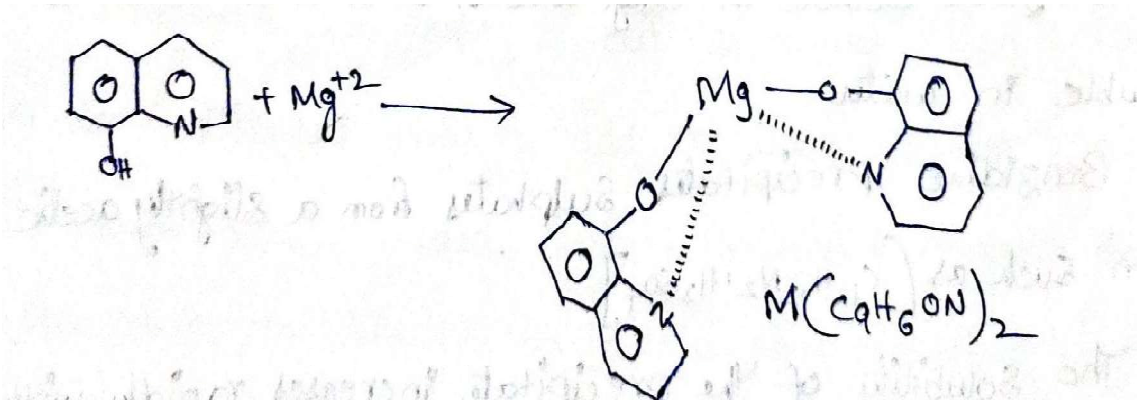
Oxine forms complex with ions coordination number 4, 6.8.

a) Examples of coordination number 4:-

Compounds are Mg, Cd, and Pd etc.

These are can be detected by using oxine.

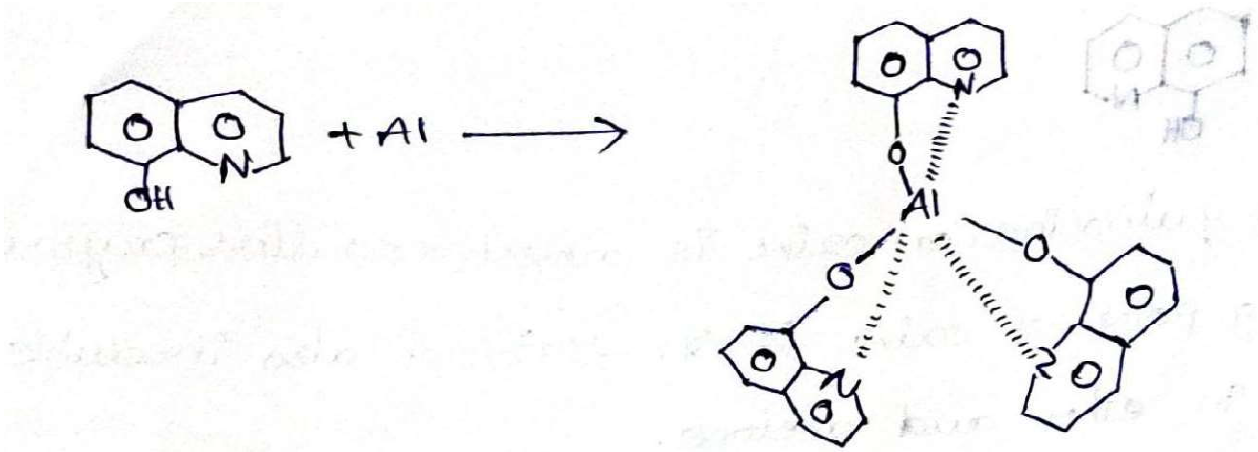
It gives complex with 'Mg^{+2}' is



b) Coordination number '6':-

Ex: - Al, Fe, Ga, Bi etc M $(C_9H_6ON)_3$

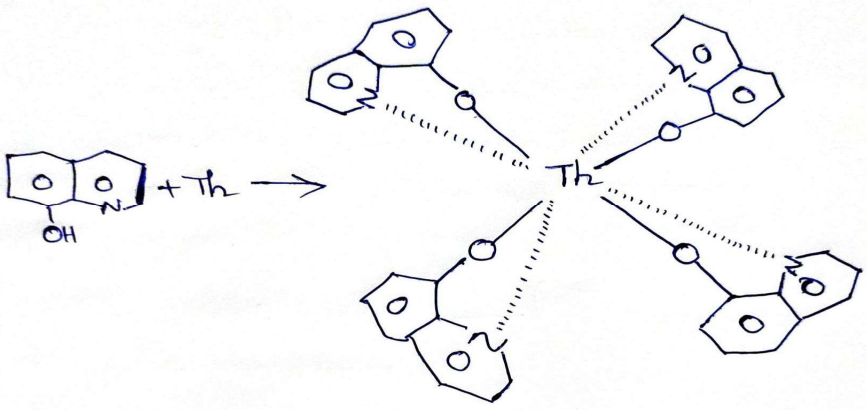
These gives complex with 'Al^{+3}' is



c) Coordination number '8':-

Ex: - Th & Zr M $(C_9H_6ON)_4$

These gives complex with 'Th' is



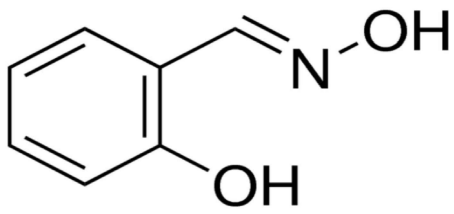
3. Benzidine:-

Structure:-

Benzidine is soluble in ethyl alcohol and ether, which is insoluble in water. Benzidine precipitates sulphates from a slightly acetic medium such as [$C_{12}H_{12}N_2$ H_2SO_4]. Here if the solubility of precipitate is increases when the rapidly with the temperature.

4. Salicyaldoxime:-

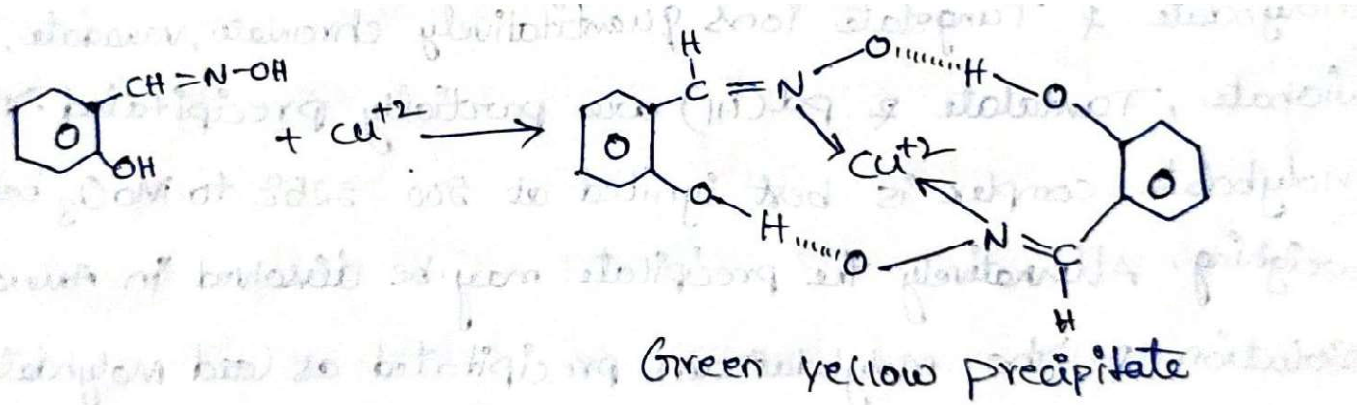
Structure:-



Preparation of solution:-

It is soluble in acetone, ether & ethyl alcohol. Dissolve 1g of reagent in 5mL of ethyl alcohol & pour slowly with stirring 90mL of water at 80°c. It is employed for the determination of copper; a green yellow colour precipitate is formed.

It is obtained in the presence of acetic acid preparation is complete at pH=2.4-2.6. After precipitation is completed the precipitate is weighed & Ignited at 100-120°C.



Procedure:-

To take 10-100mg of Cu^{+2} substance, which is dissolved in 100mL distilled water & add 2M NaOH solution & add 1.5mL dil. acetic acid & added freshly prepared reagent solution. After then to this added 1% salicylaldoxime solution is slightly excess is added at room temperature. Then it gives precipitate. It is washed with dil. acetic acid & then to taken in to a crucible & Ignited at 100°- 120°C & weighed as a precipitate.

5) Benzoin oxime / Benzoin α - oxime / cupron:-

This compound yields as a green precipitates ($CuC_{14}H_{11}O_2N$), with copper in dilute ammonia solution, which may be dried to constant weight at 100°c. Ions which are precipitated by aqueous ammonia are kept in solution by the addition of tartrate. The reagent is then specific for copper. Copper may thus be separated from cadmium, lead, Nickel, cobalt, Zinc, aluminum and small amount of iron.

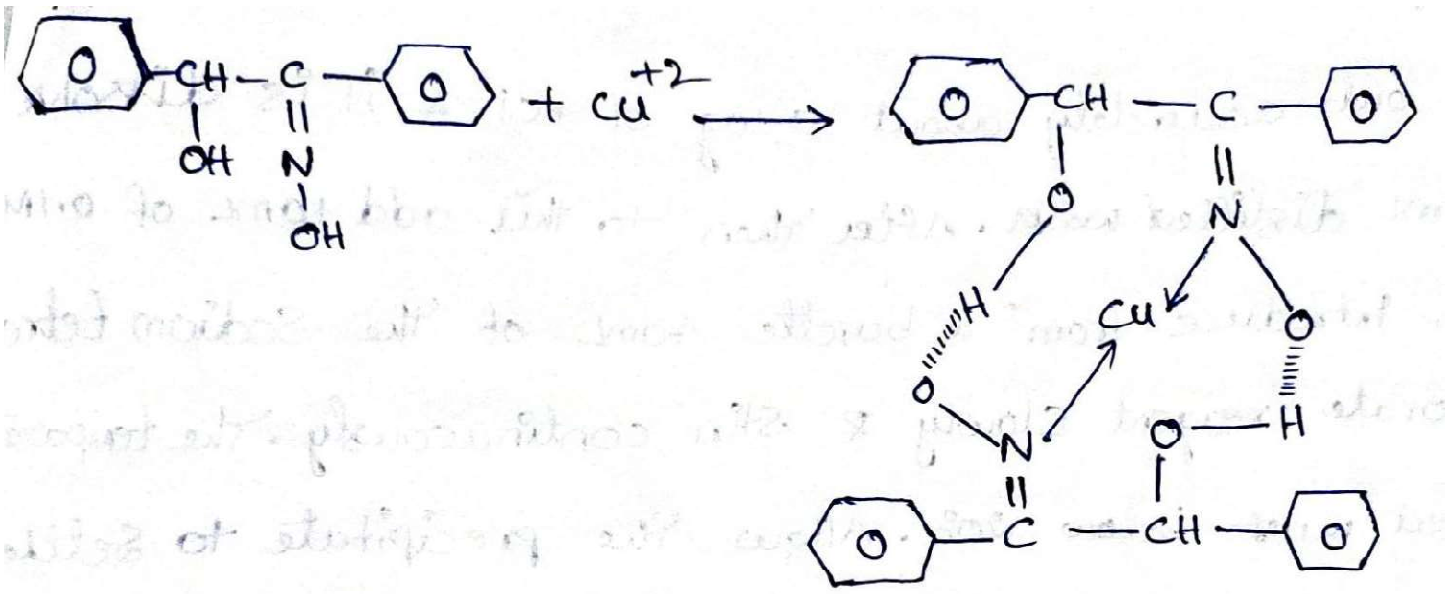
Structure:-

From strongly acidic solutions benzoin α-oxime precipitates, molybdate & tungstate ions quantitatively chromate, vanadate, & Pd (III) partially precipitated. The molybdate complex is best ignited at 500- 525% to MoO_3 before weighing. Alternatively the precipitate may be dissolved in ammonia solution & the molybdenum precipitated as leads to molybdate in which form it is conveniently weighed.

Benzoine α- oxime is a white crystalline solid. The melting point is 152°c. In which is sparingly soluble in water but fairly soluble in ethanol. The reagent employed as a 2% solution in ethanol.

The benzoin α-oxime forms complex with copper is,

Equation:-



It contains 22. 01% of copper is drying at 110°c.

6. Sodium tetra phenyl boron (or) potassium tetra phenyl borate: -

A solution of sodium tetra phenyl borate Na (B $(C_6H_5)_4$) is probably the best precipitant for potassium, but it is expensive. Precipitate may be affected at a temperature below 20°c in dilute mineral acid solution (pH-2) in which interference from most foreign ions is negligible. The precipitate is granular & settles rapidly. It is washed with a saturated aqueous solution of the precipitate & the potassium tetra phenyl Borate (TPB) is dried at 120°c & weighed. The compound decomposes at temperatures above 265°c. The precipitate of constant composition K [B (C_6H_5)] and is sparingly soluble in water (5.1 mg of K at 20°). A very few elements are interferes with the determination. These include the ions of silver, mercury (II) Thallium (I), rubidium and cesium, ammonium ion, which forms a slightly soluble salt, can be removed by ignition prior to the addition of the reagent.

Procedure:-

Accurately weighed 0.10g of KCl & It is dissolved it in 50 ml distilled writer. Then to this add 10 ml of 0.1 M HCl. Then introduce from a burette 40 ml of the sodium tetra Phenyl borate reagent slowly & stir continuously the temperature throughout must below 20°c. Allow the precipitate to settle during one hour. Collect the precipitate on a sintered glass filtering crucible, wash the precipitate with a small volume (5-10 ml in small portions) of saturated potassium tetra phenyl borate solution & finally with 1-2mL ice cold distilled water. Dry at 120°c & cool the covered crucible in a desiccators. Weighed as K [B $(C_6H_4)_4$].

7) Tetra phenyl arsinium Chloride: - As [(C6H5)4] Cl: -

If any ions forming a precipitate with tetra phenyl arsinium chloride (e.g. MnO_4^-, ClO_4^-, Br^-, I^-, IO_3^- & SCN^-) with Interferences.

Di fluoro phosphates give slight interference which can be overcome by boiling the solution for a few minutes to hydrolysis di fluoro phosphate, the hexa fluoro phosphate ion is not affected by the treatment.

Procedure: -

To an aliquot containing 36-55mg of potassium hexa fluoro phosphate & aqueous ammonia until the solution is basic. A final concentration of ammonia in the range 5-10 M is satisfactory and the total volume of solution should be to about 50ml.warm to about 50°c & add about twice the equivalent amount of 0.015 M tetra phenyl arsinium chloride slowly & with stirring. Allow to stand for 30 minutes. Filter through a medium. Porosity sintered glass filter & with 5-10mL portions of dilute aqueous ammonia, dry the precipitate to constant weight at 105-115% and weigh as $(C_6H_5)_4 AsPF_6$.

C) Electro-gravimetric analysts:-

In this method is used to separate & quantify ions of a substance, usually a metal. In this process the analyte solution is electrolyzed. Electro chemical reduction causes the analyte to be decomposed on the cathode. It is a one of electro chemical analytical method the electro analytical techniques that can be determine anion (or) molecule by direct measurements.

Principle:-

In the electro gravimetric processes the analyte element is weighed after it has been de electrolytic ally deposited up on a suitable electrode.

Theory:-

Electrode deposition is governed by ohm's law and by faraday's two laws of electrolysis.

Ohm's law:-

Ohm's law expresses the relation b/w the three fundamental quantities they are current, resistance & electromotive force. The current (i) is directly proportional to the electromotive force (E) and inversely proportional to the resistance (R).

$$i=E/R$$

Faraday's law state:-

The amount of substance liberated at the electrodes of a cell is directly proportional to the quantity of electricity which passes through the solution.

The amount of different substances liberated (or) dissolved by the same quantity of electricity are proportional to the relative atomic masses divided by the number of electrons involved in the respective electrode processes.

Important terms in electro gravimetry:-

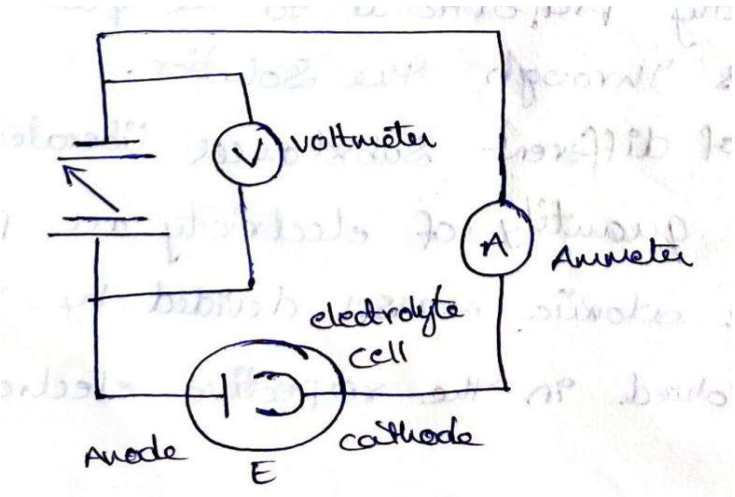
Electro gravimetry apparatus:-

Electro gravimetry is carried out in our electrolytic cell. This consists of two electrodes with an external electric energy supply the two main parts of the system are the electrodes.

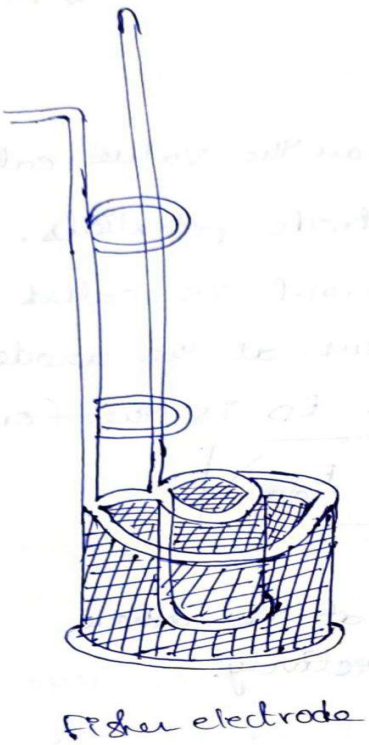
The cathode is the electrode on which metal deposition occurs due to reduction of the ions, it is attached to the negative terminal & of the energy source. The anode is the electrode at which oxidation occurs. It is attached to the positive terminal of the energy source. The cathode and anode is illustrated in the figure.

The electrodes are made of platinum gauze as the open construction assists the circulation of the solution. Then they made for the concentration of the electrolysis current to this electrode.

Typical electrodes are the fisher type a glass tube is slid in to the loops on the wire of the outer electrode and the wire to the inner electrode passes through this tube. It is necessary to know the current density for a particular determination.



Besides the electrodes, the circuit also requires a. d. c current sources rated at 3-15V, a variable resistance, and an ammeter a voltmeter, a magnetic stirrer and a hot plate. All these components are provided in commercial electrolysis units and a may sometimes include a spinning inner electrode to assist in stirring the solution undergoing electrolysis.



Decomposition voltage or decomposition potential:-

The point at which the current is suddenly increases in evident & in this instance it is at about 1.7V. The potential at this point is called decomposition potential.

We may define the decomposition potential of an electrolyte as the minimum external potential that must be applied in order to bring about continuous electrolysis. The phenomenon of polarization exerts a back EMF in electrolysis, which reduces the actual EMF of the cell.

The applied voltage which is just sufficient to overcome the back EMF due to polarization and also to bring about the electrolysis of an electrolyte without any hindrance is known as decomposition potential. The decomposition potential Ed is composed of various potentials and is given by,

$$\mathbf{Ea\ (min) = Ed = Eb + Es + Ev}$$

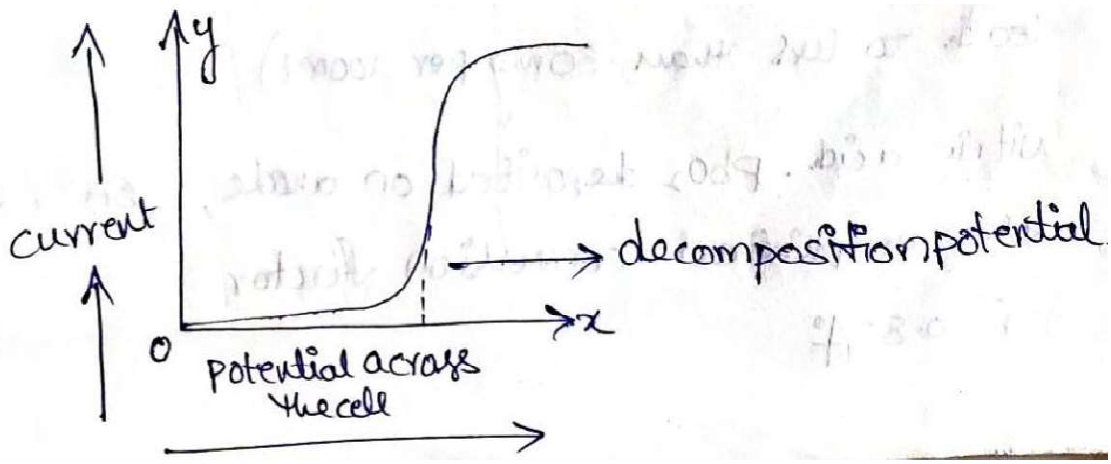
Where,

Ea=Applied potential

Ed=Decomposition potential

Eb=Theoretical counter or back potential

Ev=Overvoltage



Over voltage or over potential and their importance:-

In electrochemistry, over potential is the potential difference (voltage) between a half-reaction's thermodynamically determined reduction potential and the potential at which the Redox event is experimentally observed.

The term is directly related to a cell's voltage efficiency.

The excess potential required for the discharge of an ion at an electrode over and above the equilibrium potential of the electrode. 2: voltage in excess of the normal operating voltage of a device or circuit.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an overvoltage, represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface.

It many instances higher than the value calculate from the difference of the reversible electrode potentials. The excess voltage over the calculated back e. m. f is called the over potential. Over potential may occur at the anode as well as the cathode. The de composition voltage ED is their fore

ED = E cathode + E o c - (E anode + E o a)

Where,

E o c & E o as are the over potential at the cathode and anode respectively.

Instrumentation:-

Principle:-

The main principle involved in this method is the deposition of the solid on an electrode from the analyte solution. Explain the principle of electro gravimemetry. There are types of electro gravimemetric method.

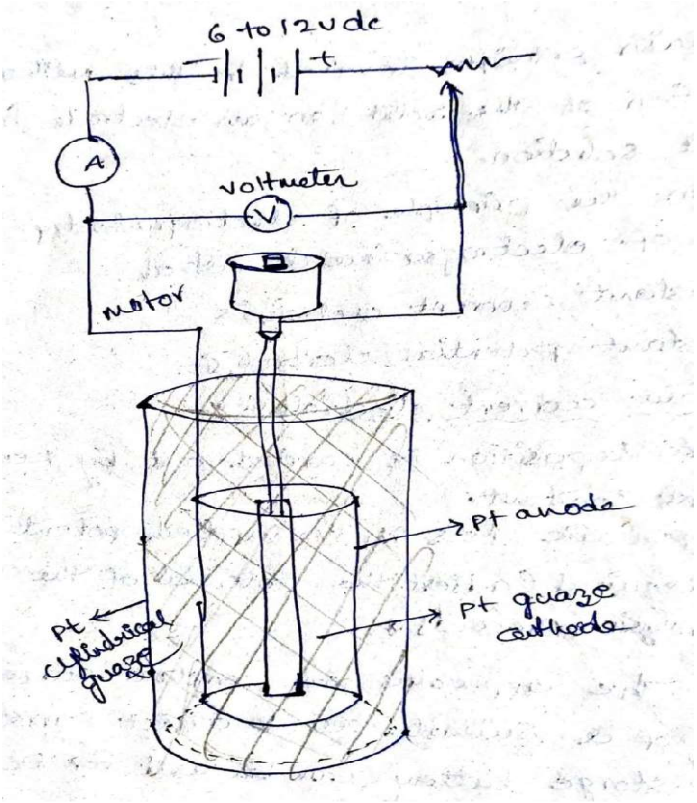
1. Constant current electrolysis (or) electrolysis at constant current

2. Constant potential electrolysis (or) electrolysis at controlled potential

1. Constant current electrolysis:-

Electro deposition is carried out by keeping current constant. Here periodic increases in the applied potential are required (adjust the potential of the cell) as electrolysis proceeds. The apparatus for constant current electrolysis consists of a

suitable cell & direct current source. A 6V storage battery can be used for DC power source. An ammeter & voltmeter are used to indicate the current & applied voltage respectively. The voltage applied to the cell is controlled by a resistor. The cathode is usually cylindrical platinum quartz.



Determination of Cu^{2+} by constant current electrolysis:-

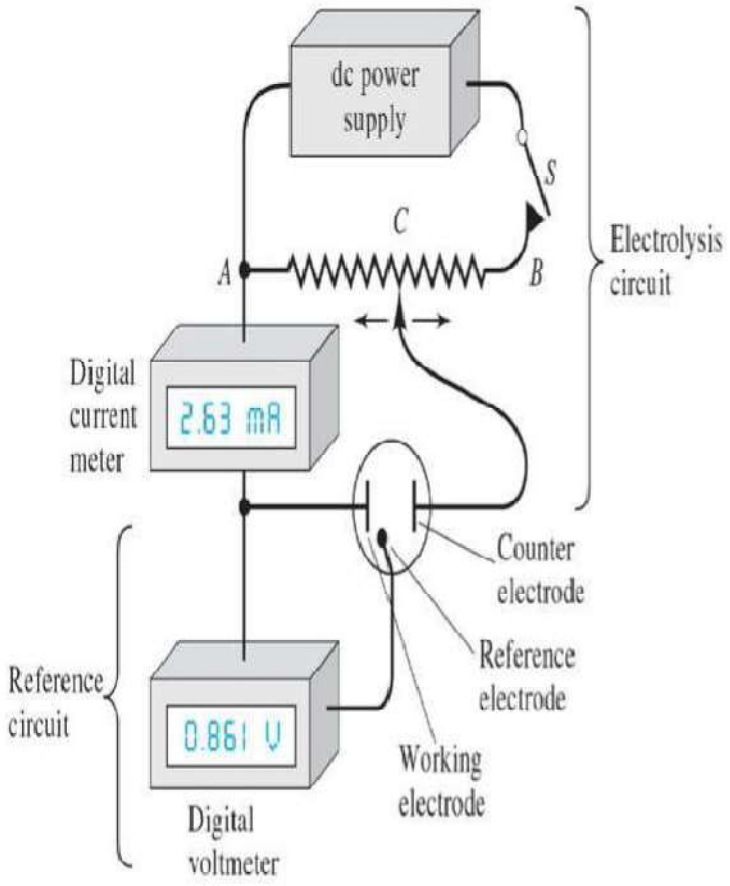
Cu^{2+} is decomposed by conc. H_2SO_4 / conc. HNO_3 but in the electrolysis of Cu^{+2}, we can use the mixture of both conc. H_2SO_4 & conc. HNO_3 acids. We can supply the current of 2, 3 amps & potential of 3- 4 vs.

Procedure:-

To take 100ml solution contains 0.2-0.3 g of copper & it is decomposed with a mixture of 2 ml of conc. H_2SO_4 & 1 ml of conc. HNO_3, then this solution is an electrolyte solution. In electrolyte solution a pair of platinum (cathode + anode), then 80% of solution is dipped then current is applied to 2-3 amps & 3-4v used. Then blue colour is disappearing. Then reduced 0.5-1 amp for 10-15min electrolyzed, and then cathode is removed, washing thoroughly & dipped in distilled water. Then dried at 110^0C for 3min & cool the solution for 5min & weighed, then cathode to gives a cu^{+2} solutions.

2) Constant potential electrolysis:-

It is possible to separate two elements whose deposition potentials differ sufficiently (By a few tenths of a volt). The potential of the cathode is controlled so that it never becomes sufficiently negative to allow the deposition of the next element. As can be seen from the potential of the centered becomes negative (due to concentration polarization) & that co-deposition of the other species beings begins before the analytic is completely deposited.



Apparatus for controlled-potential, or potentiostatic, electrolysis. Contact *C* is adjusted as necessary to maintain the working electrode (cathode in this example) at a constant potential. The current in the reference electrode is essentially zero at all times. Modern potentiostats are fully automatic and frequently computer controlled. The electrode notations in the figure are the currently acceptable notations.

Determination of Copper & Lead, Tin in brass and bronze by controlled potential electrolysis:-

Electrolysis method:-

Dilute the filtrate from the tin (Sn) determination and then to this added approximately 200mL of concentrated HNO_3. The solution contains then to this added 10% of 10mL of concentrated H_2SO_4 is approximately. After electrolyte the solution in a beaker, starting with a current of 2 amps & gradually working up to 3 amps. In the blue colour of the solution is disappear, using either a rotating anode (or) rotating cathode and continuous the electrolysis for 45min at the end of this time stop the rotation of the electrode but do not turn of the electrolysis current. Lower the beaker & switch of the current just before the electrodes come out of the solution quickly wash the electrodes with distilled water from a wash bottle. Remove and immerse immediately in methyl alcohol. Then burn of the alcohol in the air keeping the electrodes in constant motion cool in desiccators and weighed. The cathode contains copper in the metallic state and anode contains the Lead as Lead oxide. Calculate the later to lead. Test the solution for complete removal of copper and lead by electrolysis with fresh electrodes. The difference is the weights of electrodes represent the amount of copper and lead percentage present in the sample.

$$\% \text{ Lead} = \frac{\text{Weight of } PbO_2 \text{ X } 0.8643}{\text{Total weight of the sample X } 100}$$

Applications:-

Conditions for determine metals by electrogravimetry:-

S.NO	Ion	Electrolyte	Electrical details
1	Cd^{+2a}	Potassium cyanide forming $K_2[Cd(CN)_4]$	1.5 to 2A, 2.5 to 3V
2	Co^{2+a}	Ammonical sulphate	4A, 3 to 4V
3	Cu^{2+}	Sulphuric acid- nitric acid	2 to 4A, 3 to 4V
4	Pb^{2+a}	Tartrate buffer or chloride solution(solubility limits the amount of lead to less than 50mg per 100mL)	2A, 2 to 3V
5	Pb^{+2}	Nitric acid, PbO_2 deposited on anode, use empirical conversion factor of 0.86A	5A, 2 to 3V
6	Ni^{2+a}	Ammonical sulphate	4A, 3 to 4V
7	Ag^{+}	Potassium cyanide forming $K[Ag(CN)_2]$	0.5 to 1.0A, 2.5 to 3V
8	Zn^{2+a}	Potassium hydroxide solution	4A, 3.5 to 4.5V

Simple electrolytic separations:-

S.NO	Ion	Electrolyte	Electrical details
1	Cu/Ni	Deposit 'Cu' from H_2SO_4 solution neutralize with NH_3 add 15mL conc. NH_3(Aq) deposit 'Ni'	2 to 4A, 3 to 4V 4A, 3 to 4V
2	Cu/Pb	Nitric acid solution deposit 'Cu' on cathode, PbO_2 on anode.	1.5 to 2A, 2V

Examples of controlled cathode potential determination:-

S.NO	Metal	Electrolyte	E cathode (VS) SCE(V)	Separation form
1	Sb	Hydrazine- HCl	-0.3	Pb, Sn
2	Cd	Ethanoate buffer	-0.8	Zn
3	Cu	Tartrate-hydrazine-Cl^-	-0.3	Bi, Cd, Pb, Ni, Sn, Zn
4	Pb	Tartrate-hydrazine-Cl^-	-0.6	Cd, Fe, Mn, Ni, Sn, Zn
5	Ni	Tartrate- NH_4OH	-1.1	Al, Fe, Zn
6	Ag	Ethanoate buffer	+0.1	Cu, heavy metals

UNIT-III

REDUCTANT SYSTEM – PRINCIPLES AND APPLICATIONS IN ANALYSIS

Oxidation:-

Loss of electron is called Oxidation, Loss of Hydrogen and Gain of Oxygen is called Oxidation.

Ex:-Fe (II) $\rightarrow$Fe (III) + e^-

Reduction:-

Gain of electrons is called Reduction, Gain of Hydrogen and Loss of Oxygen is called Reduction.

Ex:-Fe (III) $\rightarrow$Fe (II)

Oxidant:-

Oxidant means itself reduced other substance will be oxidized.

Mn (VII) +Fe (II) $\rightarrow$Mn (II) +Fe (III)

Reductant:-

Reductant means itself oxidized other substance will be reduced.

Mn (III) $\rightarrow$Mn (II)

Oxidizing agent:-

Cause the oxidation of another substance.

$AgNO_3$ is the oxidizing agent

Reducing agent:-

Cause the reduction of another substance. Cu is the reducing agent.

Oxidizing agent becomes reduced and the reducing agent becomes oxidized.

$$Cu + 2AgNO_3 \rightarrow CuNO_3 + 2Ag$$

Redox reaction:-

An Oxidation-Reduction is any chemical reaction in which the oxidation number of a molecule, atom, (or) ion changes by gaining (or) losing an electron. The formation of Hydrogen Fluoride is an example of a Redox reaction. We can break the reaction down to analyze the Oxidation and Reduction of reactants.

Reductant properties:-

Electrode potential:-

This is tendency of electrode to gain (or) loss of the electrons. Then it is contact with its own ion in solution is called electrode potential. It is depends up on nature of the metal concentration and temperature of the solution. There are 3 types, there are,

1) Standard potential:-

The potential is measured at 25^0C, one atmospheric pressure and ions are having unit activity. It is called standard potential.

The E^0 of electrode with 1M (or) 1N solution of the ions and one atmospheric pressure (if there is gas) is measured with reference to normal Hydrogen electrode (used as cathode) the potential is orbital taken as 'ZERO'. The normal hydrogen electrode also called as standard hydrogen electrode.

$$E = E^0\text{-}RT/nF \log Oxi / red^n$$

At unit activity,

$$E = E^0\text{-}RT/nF \log [Oxi / Oxi]$$

$$E = E^0\text{-}RT/nF \log (1)$$

$$E = E^0\text{-}RT/nF (0)$$

$$E = E^0$$

E^0 = Standard potential

II) Normal potential:-

The potential developed at the electrode it is dipped in the 1N solution is called Normal potential.

$$E = E^0\text{-}RT/nF \log [Oxi/Red^n]$$

Here,

E = Normal potential

III) Formal potential:-

The potential developed at the electrode, the electrode is dipped on the formal solution (formula weight substance dissolved in water formal is molar).

Indicators:-

The substance which indicates the end point of particular reaction undergoing a colour change at end point is called indicator.

Types of indicators:-

I) Acid base indicator

II) Redox indicators

III) Complex metric indicators

IV) Instrumental indicators

V) Self indicators

I) Acid base indicator:-

The substance which indicates the end point of acid- base reaction by undergoing a colour change at end point is called acid base indicator. Every indicator has its own pH range.

Indicators	pH range	Colour change
Methyl Orange	3.2- 4.7	Pink-Yellow
Methyl Red	4.4- 6.0	Red-Yellow
Phenol Red	6.8- 8.4	Yellow-Red
Phenolphthalein	8.3-10.0	Colourless-Pink

Methyl orange:-

It is a weak Organic base.

$Me\ OH \rightarrow Me^{+} + OH^{-}$

In the basic medium is -Yellow. In the acidic medium is -Pink.

Phenolphthalein:-

It is a weak Organic acid.

$H\ ph \rightarrow H^{+} + ph^{-}$

Selection of indicators:-

Titration	pH range end point	Indicator
Strong acid VS Strong base	3-10	Any indicator
Strong acid VS Weak base	3-7	Methyl Orange, Phenyl red, Phenol red
Weak acid VS Strong base	7-10	Phenol red, Phenolphthalein
Weak acid VS Weak base	No sharp change at end point	No indicator

II) Redox indicators:-

The substance which indicates the end point is Oxidant-Reductant reaction by undergoing a colour change the end point is called Oxidant- Reductant (or) Redox indicators.

Ex:-DPA, N- Phenyl Anthranilic acid, Ferroin, Starch, Di Methyl Ferroin.

III) Complex metric indicators:-

The substance which indicates the end point of metal complexing agent reactions (ligand) by undergoing a colour change the end point is called complex metric indicators.

Ex:-EBT, Solo Chrome black-T, Murexide.

IV) Instrumental indicators:-

They are two types.

I) Reference electrode- Calomel electrode

II) Indicator electrode- Platinum electrode

V) Self indicators:-

Self indicators acts as a colour change at the end of the reaction majored coloured substance acts as a self indicators.

Ex:-$KMnO_4$, Ceric Sulphate

a) Inorganic systems:-

i) Cr (II):-

Divalent chromium compounds are exhibits in strong reducing agent. Titration with Cr (II) salt solution is known as chromo metric titrations.

Cr (II) is good reductant. It is itself oxidized other substance will be reduced.

Cr (II) salts are used in the determination of in inorganic metal ions.

$$Cr\ (II) \rightarrow Cr\ (III) + 1e^-$$

The normal Redox potential value is -0.421V. The Redox potential value is changes very little with various media like HCl, H_2SO_4, and CH_3COOH.

$$HCl \rightarrow -0.395V$$

$$H_2SO_4 \rightarrow -0.412V$$

$$CH_3COOH \rightarrow -0.403V$$

Preparation of $K_2Cr_2O_7$ solution:-

Dissolve 40g of $K_2Cr_2O_7$ in 200ml of distilled water & then to this added 15ml of concentrated H_2SO_4. Reduced to solution by the passing SO_2 & then to this added diluted to 250ml water & electrolyte the solution with constant stirring. Applied potential volts 50V current is 0.02amp. Then the reduction process is 7-12hrs. Finally required solution is stored in amber coloured bottle.

Stability:-

Chromium ions very easily oxidized by air. Then the solution must be stored & delivered from the burette & under an inert gas & the solution being titrated must be completely free from dissolved oxygen.

$$4Cr^{+2} + O_2 + 4H^+ \rightarrow 4Cr^{+3} + 2H_2O$$

Standardization of Cr (II) by using standard Fe (III):-

Cr (II) present in the sample, in this determination of Cr (II) is standardized by the standard Fe (II) solution.

$$Cr\ (II) + Fe\ (III) \rightarrow Cr\ (III) + Fe\ (II)$$

Procedure:-

To take 10ml of sample is taken into a 250ml conical flask. After then added 10ml water & 5ml of H_2SO_4 & 3ml of H_3PO_4 & 2 (or) 3 drops of DPA indicator. The above solution is titrated with Fe (III).

Indicators: - DPA, P- Hydroxyl crystal, Ferroin, Methyl red.

Applications:-

1) Determination of Sn (II):-

To take Sn (II) solution & then to this added excess amount of $KMnO_4$,then to form a Sn (IV) & Mn (II). The untreated manganese is titrated with $K_2Cr_2O_7$ solution.

$$Sn\ (II) + Mn\ (VII) \rightarrow Sn\ (IV) + Mn\ (II)$$

$$Mn\ (VII) + Cr\ (II) \rightarrow Mn\ (II) + Cr\ (III)$$

2) Determination of Mo (VI):-

To take 10ml Mo (VI) sample solution. After then to this added 10ml of distilled water & 2 (or) 3 drops of DPA indicator. Then it is titrated with standard Cr (II) solution.

$$Mo\ (VI) + Cr\ (II) \rightarrow Mo\ (V) + Cr\ (III)$$

3) Determination of Mn (II):-

To take 10ml Mn (II) sample solution. Then to this added 10ml of distilled water & 2 (or) 3 drops of DPA indicator & then to this added excess amount of Fe (III). The untreated Fe (III) is titrated with Cr (II) solution.

$$Mn\ (II) + Fe\ (III) \rightarrow Mn\ (VII) + Fe\ (II)$$

$$Fe\ (III) + Cr\ (II) \rightarrow Fe\ (II) + Cr\ (III)$$

ii) V (II):-

V (II) is good reducing agent. It is itself oxidized other substance will be reduced.

V (II) salts are used in the determination of in quantitative analysis.

$$V\ (II) \rightarrow V\ (III) + 1e^-$$

The normal potential of Redox potential value is -0.255V at 25^0C.V (V) solution mostly carried out in the acid medium like H_2SO_4, HCl, and CH_3COOH.

Preparation of V (II) solution:-

Dissolve sufficient amount of Ammonium Meta Vanadate is dissolved in hot water in the presence of acidic medium. It is reduced to V (II) by adding Zn-Hg to the sample solution. Then required solution is stored in an amber colour bottle.

Stability:-

The V (II) solution in 10N H_2SO_4 is stable for one hour in an open burette. It is however an established fact that is easily oxidized by an air and the solution is stored and delivered from the burette under inert gas which is usually hydrogen. Furthermore the being titrated must be 100% free from dissolved oxygen.

$$4V\ (II) + O_2 + 4H^+ \rightarrow 4V\ (III) + 2H_2O$$

In the presence of some impurities are readily react with hydrogen ion tends to liberation the hydrogen gas.

$$2V\ (II) + 2H^+ \rightarrow 2V\ (III) + H_2\uparrow$$

Standardization of V (II) by using Fe (III) solution:-

To take 10ml V (II) solution is taken in to a 250ml conical flask & then to this added 10ml water & 2 (or) 3 drops of Phenazone frame as an indicator. Then this solution is titrated with Fe (III) solution.

$$V\ (II) + Fe\ (III) \rightarrow V\ (III) + Fe\ (II)$$

Indicators: - Phenazone frame, N- Phenyl Anthranilic acid, SCN^-, Methyl red.

Applications:-

1) Determination of Cu (II):-

To take the 10ml of Cu (II) solution is taken in to a 250ml conical flask and then to this added 10ml of distilled water and 2 (or) 3 drops of N-Phenyl Anthranilic acid as an indicator. The above mixture is titrated with V (II) solution.

$$Cu\ (II) + V\ (II) \rightarrow Cu\ (I) + V\ (III)$$

2) Determination of Cr (VI):-

To take the 10ml of Cr (VI) solution is taken into a 250ml conical flask and then to this added 10ml of distilled water and 2 (or) 3 drops of methyl red as an indicator. Then this solution is titrated with V (II) solution

$$Cr\ (VI) + V\ (II) \rightarrow Cr\ (III) + V\ (III)$$

3) Determination of Ce (VI):-

To take the 10ml of Ce (IV) solution is taken in to a 250ml conical flask and then to this added 10ml of distilled water and 2 (or) 3 drops of N-Phenyl Anthranilic acid as an indicator. Then this solution is titrated with V (II) solution.

$$Ce\ (IV) + V\ (II) \rightarrow Ce\ (III) + V\ (III)$$

4) Determination of Mn (II):-

To take the 10ml of Mn (II) sample solution is taken into a conical flask and then to this added 10ml of distilled water and then to this added excess amount of Fe (III) and 2 (or) 3 drops of DPA indicator. The untreated Fe (III) is titrated with Chromium (II) solution.

$$Mn\ (II) + Fe\ (III) \rightarrow Mn\ (VII) + Fe\ (II)$$

$$Fe\ (III) + Cr\ (II) \rightarrow Fe\ (II) + Cr\ (III)$$

iii) Ti (III):-

Ti (III) Chloride & Titanium (III) sulphate are power full reducing agent and energetic reagents because low standard potential.

Ti (III) is good reducing agent. It is itself oxidized other substance will be reduced. It is used in the determination of quantitative analysis.

$$Ti\ (III) \rightarrow Ti\ (IV) + 1e^-$$

The Redox potential value is 0.1V, by complex formation with citric & titanium system, Ti (III) by Ti (IV) much more strongly reduced.

Preparation of Ti (III) solution:-

To take 0.6g of titanium hydride (TiH_2) is taken into a 250ml volumetric flask. Then it is dissolved in concentrated H_2SO_4 in 20ml & then to this added 80ml of water, then this solution is boiling for 2min. then the solution is digesting to 100ml water, then dark colour solution is formed. Then the bottle filled with CO_2 to maintain the inert atmosphere medium.

Stability:-

Titanium salt solution on oxidized rapidly by air & should be kept out of direct sunlight. The titanium sulphate is in 4N H_2SO_4 more stable to air. $TiCl_3$ in HCl is more stable. Then titration with titanium chloride is best carried out in an atmospheric CO_2.

Standardization of Ti (III) by using $K_2Cr_2O_7$:-

To take the Ti (III) 10ml is taken into a250ml conical flask & then to this added 10ml water &5ml of 5N H_2SO_4 and 3ml of H_3PO_4 & 2 (or) 3 drops of DPA indicator & the above solution is titrated with standard $K_2Cr_2O_7$ solution.

$$Ti\ (III) + Cr\ (VI) \rightarrow Ti\ (IV) + Cr\ (III)$$

Indicators: - DPA, SCN^-, Sulfonamide.

Applications:-

1) Determination of Fe (III):-

To take the 10ml of Fe (III) solution is taken into a250ml conical flask and then to this added 10ml water and 5ml of 5N H_2SO_4 & 3ml of H_3PO_4 and 2 (or) 3 drops of DPA indicator, finally the above solution is titrated with Ti (III).

$$Fe\ (III) + Ti\ (III) \rightarrow Fe\ (II) + Ti\ (IV)$$

2) Determination of Mn (VII):-

To take the 10ml of Mn (VII) solution is taken into a250ml conical flask & then to this added 10ml water and 5ml of 5N H_2SO_4 & 3ml of H_3PO_4 & 2 (or) 3 drops of DPA indicator, finally the above solution is titrated with Ti (III).

$$Mn\ (VII) + Ti\ (III) \rightarrow Mn\ (II) + Ti\ (IV)$$

3) Determination of Cu (II):-

To take the10ml of Cu (II) solution is taken into a250ml conical flask and then to this added 10ml water and 5ml of 5N H_2SO_4 & 3ml of H_3PO_4 & 2 (or) 3 drops of DPA indicator, finally the above solution is titrated with Ti (III).

$$Cu\ (II) + Ti\ (III) \rightarrow Cu\ (I) + Ti\ (IV)$$

4) Determination of Ce (IV):-

To take the 10ml of Ce (IV) solution is taken into a 250ml conical flask and then to this added 10ml water and 5ml of 5N H_2SO_4 & 3ml of H_3PO_4 & 2 (or) 3 drops of DPA indicator, finally the above solution is titrated with Ti (III).

$$Ce\ (III) + Ti\ (III) \rightarrow Ce\ (III) + Ti\ (IV)$$

iv) Sn (II):-

Sn (II) is good reducing agent. It is itself oxidized & other substance will be reducing agent.

Sn (II) salt is used in the determination of in quantitative analysis.

$$Sn\ (II) \rightarrow Sn\ (IV) + 2e^-$$

The normal Redox potential value is -0.15V.

Preparation of Stannous (II) Chloride solution:-

To take sufficient amount of $SnCl_2$ is taken in to a 250ml volumetric flask. Then it is dissolved in sufficient amount of concentrated 1:1 HCl. Then to this added sufficient amount of $CaCO_3$ and heated gently up to CO_2 is evaporated. The solution is making up with mark with distilled water. Finally required solution is stored in an amber colour bottle.

Stability:-

To take sufficient amount of sample & it is dissolved in 1:1 HCl. Then to this added $CaCO_3$ & heated up to CO_2 gas to maintain the inert atmosphere medium. Then the solution is stored in an amber colour bottle.

Standardization of Sn (II) by using $K_2Cr_2O_7$:-

To take 10ml of stannous chloride solution is taken into a 250ml conical flask. Then to this added 10ml distilled water & then to this added 2 (or) 3 drops of rubrophene (or) ammonium molybdate as indicator. Then it is titrated with $K_2Cr_2O_7$ solution.

$$Sn\ (II) + Cr\ (VI) \rightarrow Sn\ (IV) + Cr\ (III)$$

It is also standardized by potassium bromated in the presence of HCl by using rubrophene as an indicator.

$$KBrO_3 + 3SnCl_2 + 7HCl \rightarrow 3SnCl_4 + KBr + KCl + 3H2O$$

Indicators: - $KSCN^-$, DPA, Rubrophene, Starch.

Applications:-

1) Determination of Sb (V):-

To take the 10ml of Sb (V) sample solution is taken into a 250ml conical flask. Then to this added 10ml distilled water & 5ml of 5N H_2SO_4 & 3ml of H_3PO_4 and then to this added 2 (or) 3 drops of rubrophene indicator. Then this solution is titrated with Sn (II) solution.

$$Sb\ (V) + Sn\ (II) \rightarrow Sb\ (III) + Sn\ (IV)$$

2) Determination of Hg (II):-

To take the 10ml of Hg (II) solution is taken into a 250ml conical flask. Then to this added 10ml distilled water & 5ml of 5N H_2SO_4 & 3ml of H_3PO_4 & then to this added 2 (or) 3 drops of rubrophene indicator. Then this solution is titrated with Sn (II) solution.

$$Hg\ (II) + Sn\ (II) \rightarrow Hg\ (I) + Sn\ (IV)$$

3) Determination of Cu (II):-

To take the 10ml of Cu (II) solution is taken into a 250ml conical flask. Then to this added 10ml distilled water & 5ml of 5N H_2SO_4 & 3ml of H_3PO_4 & then to this added 2 (or) 3 drops of rubrophene as an indicator. Then this solution is titrated with Sn (II) solution.

$$Cu\ (II) + Sn\ (II) \rightarrow Cu\ (I) + Sn\ (IV)$$

4) Determination of Mn (VII):-

To take the 10ml of Mn (VI) solution is taken into a 250ml conical flask. Then to this added 10ml distilled water & 5ml of 5N H_2SO_4 & 3ml of H_3PO_4 & then to this added 2 (or) 3 drops of rubrophene as a indicator Then this solution is titrated with Sn (II) solution.

$$Mn\ (VII) + Sn\ (II) \rightarrow Mn\ (II) + Sn\ (IV)$$

v) Fe (II):-

Fe (II) is good reducing agent; Fe (II) is light green colour. It is itself oxidized other substance will be reducing agent.

Fe (II) salt is used in the determination of in quantitative analysis. The Redox potential value is 1.24V.

$$Fe\ (II) \rightarrow Fe\ (III) + 1e^-$$

Preparation of Fe (II):-

Accurately weighed sufficient amount of Fe (II) is dissolved in 1:1 H_2SO_4. Then it is taken into a 250ml volumetric flask. This solution is stored in an amber colour bottle to maintain the acidic medium.

Stability:-

The above solution is taken in to amber colour bottle and passes CO_2 gas and to maintain the inert atmosphere (or) acidic medium.

Standardization of Fe (II) by using $K_2Cr_2O_7$:-

To take the 10ml of Fe (II) sample solution is taken into a conical flask. Then to this added 10ml distilled water & 5ml of 5N H_2SO_4 & 3ml of H_3PO_4 & then to this added 2 (or) 3 drops of DPA indicator. Finally the above solution is titrated with $K_2Cr_2O_7$ solution.

$$Fe\ (II) + Cr\ (VI) \rightarrow Fe\ (III) + Cr\ (III)$$

Indicators:-DPA, Starch, KSCN

Applications:-

1) Determination of V (V):-

To take the 10ml of V (V) solution is taken into a 250ml conical flask. After then to this added 10ml of distilled water and 2 (or) 3 drops of DPA indicator, then this solution is titrated with Fe (II).

$$V\ (V) + Fe\ (II) \rightarrow V\ (IV) + Fe\ (III)$$

By Potentiometrically :-(Graph)

To take the 10ml of V (V) solution is taken in to a100ml beaker, then to this added 10ml of distilled water. Then this solution is introduced into potentiometrically, then to this added Fe (II) solution by drop wise.

$$V\ (V) + Fe\ (II) \rightarrow V\ (IV) + Fe\ (III)$$

2) Determination of Cu (II) :-(Graph)

To take the 10ml of Cu (II) solution is taken in to a100ml beaker, after then to this added 10ml of distilled water. Then this solution is introduced into potentiometrically, then to this added Fe (II) solution by drop wise.

$$Cu\ (II) + Fe\ (II) \rightarrow Cu\ (I) + Fe\ (III)$$

3) Determination of Ce (IV) :-(Graph)

To take the 10ml of Ce (IV) solution is taken in to a100ml beaker, then to this added 10ml of distilled water. Then this solution is introduced into potentiometrically, then to this added Fe (II) solution by drop wise.

$$Ce\ (IV) + Fe\ (II) \rightarrow Ce\ (III) + Fe\ (III)$$

4) Determination of Mn (VII) :-(Graph)

To take the 10ml of Mn (VII) solution is taken in to a100ml beaker, then to this added 10ml of distilled water. Then this solution is introduced into potentiometrically, then to this added Fe (II) solution by drop wise.

$$Mn\ (VII) + Fe\ (II) \rightarrow Mn\ (VII) + Fe\ (III)$$

vi) Hydrazine:-

Hydrazine and its derivatives are well known active reductants and these are used in the preparative organic & inorganic chemistry.

In acidic medium the reaction is as follows.

$$N_2 + 4H^+ + 4e^- \rightarrow N_2H_4$$

The Redox potential value is -0.65V in acidic medium.

In basic medium the reaction is as follows.

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^-$$

The Redox potential value of above equation is -1.16V.

Preparation of Hydrazine:-

To take sufficient amount of hydrazine sulphate is taken into a 250ml of volumetric flask. Then it is dissolved in hot water. Finally the solution is stored in an amber colour bottle then maintaining the inert atmospheric medium.

Indicators:-

Potentiometric end point is preferable but few visible indicators are also used for end point detection. In the various detections in those indicators is starch, chemiluminesence.

Standardization of hydrazine by using chloramine-T:-

Hydrazine solution is standardized by against standard chloramine – T in the presence of Na_2CO_3 solution & iodine in starch as indicator.

$$N_2H_4+2CH_3C_6H_4SO_2N\ NaCl \rightarrow N_2+2CH_3C_6H_4SO_2NH_2+2NaCl$$

Applications:-

1) Determination of halogens:-

Acidic medium:-

$$N\mathbf{2}H_4+Cl_2+H^+ \rightarrow N_2+4H^++4e^-+4Cl$$

Basic medium:-

$$N_2H_4+Cl_2+OH^- \rightarrow N_2+4H_2O+4e^-+2Cl^-$$

2) Determination of $[Fe\ (SCN)_6]^{3+}$:-

To take the 10ml of Fe (III) solution is taken into a conical flask. Then to this added 10ml of water & 5ml of 5N H_2SO_4 & 3ml of H_3PO_4 & 2 (or) 3 drops of starch indicator, then this solution is titrated with hydrazine solution.

$$N_2H_4+Fe\ (III)+H^+ \rightarrow N_2+4H^++Fe\ (II)$$

3) Determination of Cu (II):-

To take the 10ml of Cu (II) solution is taken into a conical flask. Then to this added 10ml of water & 5ml of 5N H_2SO_4 & 3ml of H_3PO_4 & 2 (or) 3 drops of starch indicator, then this solution is titrated with hydrazine solution.

$$N_2H_4+Cu\ (II)+H^+ \rightarrow N_2+4H^++Cu\ (I)$$

b) Organic systems:-

i) Hydroquinone:-

It is a powerful reducing agent. It is itself oxidized and other substance will be reduced.

Hydroquinone oxidized to Quinine.

$$C_6H_4\ (OH)_2 = C_6H_4O_2+2H^++2e^-$$

The Redox potential value is +0.68V.

Preparation of 0.1N hydroquinone:-

To take 5.50g of hydroquinone is dissolved in a hot water.

Stability:-

The solution becomes a more stable in HCl (or) H_2SO_4 is added given a 1% of concentration.

Indicators: - DPA, Ferroin, potentiometrically platinum electrode.

Standardization of hydroquinone by using $K_2Cr_2O_7$:-

Hydroquinone solution is standardized by against dichromate solution in 20% H_2SO_4 by using DPA indicator.

$$Cr\ (VI) + C_6H_4\ (OH) + H^+ \rightarrow Cr\ (III) + C_6H_4O_2$$

Applications:-

1) Determination of Ce (IV):-

To take the 10ml of Ce (IV) solution is taken into a 250ml of conical flask, then to this added 10ml of H_2O & 10ml of 20% of H_2SO_4. Then to this added 2 (or) 3 drops of DPA indicator, then this solution is titrate with hydroquinone solution.

$$Ce\ (IV) + C_6H_4\ (OH) + H^+ \rightarrow Ce\ (III) + C_6H_4O_2$$

2) Determination of V (V):-

To take the 10ml of V (V) solution is taken into a 250ml of conical flask, then to this added 10ml of H_2O & 10ml of 20% of H_2SO_4. Then to this added 2 (or) 3 drops of DPA indicator, then this solution is titrate with hydroquinone solution.

$$V\ (V) + C_6H_4\ (OH) + H^+ \rightarrow V\ (IV) + C_6H_4O_2$$

3) Determination of Cu (II):-

To take the 10ml of Cu (II) solution is taken into a 250ml of conical flask. Then to this added 10ml of H_2O and 10ml of 20% of H_2SO_4 is added, Then to this added 2 (or) 3 drops of DPA indicator, then this solution is titrate with hydroquinone.

$$Cu\ (II) + C_6H_4\ (OH) + H^+ \rightarrow Cu\ (I) + C_6H_4O_2$$

ii) Ascorbic acid:-

Structure:-

It is easily soluble in water (above 1g in 3ml of water). In aqueous solution it exhibits strong reducing agent. Ascorbic acid oxidized to form a dehydro ascorbic acid. The Redox potential value is 0.185V at pH-7.

$$C\text{-}C{=}C\text{-}CH\text{-}CH\text{-}CH_2 = C\text{-}C\text{-}C\text{-}CH\text{-}CH\text{-}CH\text{-}CH_2 + 2H^+ + 2e^-$$

Preparation of 0.1N ascorbic acid solution:-

Dissolve 8.806g of pure ascorbic acid in metal free distilled water & diluted to one liter add stability substances to the solution before dilution or store under an inert atmosphere.

Indicators:-DPA, Variamine blue, platinum electrode.

Standardization:-

Ascorbic acid solution is usually titrated against iodated (or) iodine solution. Mohr's salt can be also used as standard substance after oxidation with hydrogen peroxide (H_2O_2).

Procedure:-

Add 1g of KI to 20ml of 0.1N potassium iodide solution. Acidified with 5ml of 2N HCl & also added 2 (or) 3 drops of variamine blue indicator. Then the above solution I titrated with standard ascorbic acid.

Applications:-

1) Determination of V (V):-

To take the 10ml of V (V) solution is taken into a 250ml of conical flask. Then to this added 10ml water & 5ml of 2N HCl & also added 2 (or) 3 drops of variamine blue an indicator. Then the above solution is titrated with standard ascorbic acid.

$$V\ (V) + \text{Ascorbic acid} \rightarrow V\ (IV) + \text{de hydro ascorbic acid}$$

2) Determination of Cu (II):-

To take the 10ml of Cu (II) solution is taken into a 250ml of conical flask, then to this added 10ml water & 5ml of 2N HCl & also added 2 (or) 3 drops of variamine blue as indicator. Then the above solution is titrated with standard ascorbic acid.

$$Cu\ (II) + \text{Ascorbic acid} \rightarrow Cu\ (I) + \text{de hydro ascorbic acid}$$

3) Determination of Ce (IV):-

To take 10ml of Ce (IV) solution is taken into a 250ml of conical flask, then to this added 10ml water & 5ml of 2N HCl & also added 2 (or) 3 drops of variamine blue as indicator. Then the above solution is titrated with standard ascorbic acid.

$$Ce\ (IV) + \text{Ascorbic acid} \rightarrow Ce\ (III) + \text{de hydro ascorbic acid}$$

UNIT-IV

ANALYSIS OF SOME SELECTED DRUGS

Drug:-

It is defined as the substance is used for the purpose of diagnosis, prevention, relief (or) cure of a disease in human beings (or) animals**. Ex: -** Penicillin.

It should be a not toxic. It should be have minimum side effects. It should not injury host tissues physiologically, it should be efficient. It should not make the host cells resistance to the drug, after then it is used for some times.

Drugs are broadly classified in to 2 types.

i) Chemotherapeutic agents

ii) Pharmacodynamic agents

i) Chemotherapeutic agents:-

These are drug used in the treatment & cure of specific diseases like malaria, syphilis, tuberculosis micro organisms infecting diseases, such type of drug is known as chemotherapeutic agents.

Chemotherapeutic agent attacks & destroyed the invading organic substance without injuring (or) destroyed the cell of the infecting host. Thus chemotherapeutic chemotherapy maybe defined as the treatment of disease by chemical which selectivity inhibits the growth of parasitic organisms.

The first chemotherapeutic agent is introduced by Paul Ehrlich in 1900s, where certain organic arsenic compound against cephalous.

The chemotherapeutic agents are further divided into various types:

Organic metallic therapeutics, Anti malarial

Anti bacterial (sulpha drugs), Anti bacterial (anti biotic)

Anti protozoan's, Anti fungal

Anti helminthes, Anti septic

Anti tuberculosis & anti leprosy drug

Anti neoplastic drug

ii) Pharmacodynamic agents:-

This is a group of drug, which stimulates (or) depresses (or) various functions of the body so as to provide some leave to the body without cure in the diseases. These agents are mainly used in the use of non infecting diseases to correct abnormal functional. These drugs are further classified into various types.

Non selective central nervous system modified- i.e., dispresence

Selective modifies of central nervous system. i.e., tranquillizers.

Central nervous system stimulates- i.e., dispresence

Adrenergic stimulates, blocking agents.

Here cholinergic & anti cholinergic agents.

Cardiovascular agent, Diuretics

Anesthetics, Antipyretics & analgesics

Here Anti spasmodic, anti histamines, Anti coagulants.

Therapeutic index:-

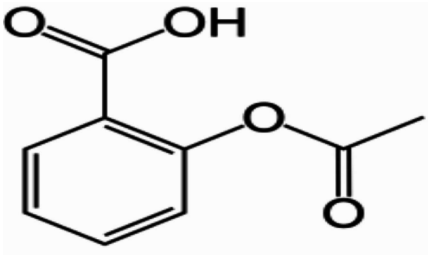
The medicinal value of the drug is generally represented by therapeutic index. This is described as the ratio of the amount necessary to kill the patient. i.e.; the maximum tolerated dose (MTD) to that required for a maximum curate dose (MCD).

$$\text{Therapeutic index} = \frac{\text{Maximum tolerated dose}}{\text{Maximum curate dose}}$$

Determinations of the following drugs are:-

1) Acetyl salicylic acid (or) Aspirin (Antipyretic - Analgesic)

Structure:-



Molecular formula:- $C_9H_8O_4$

Procedure:-

To take 1.5g of sample is taken into a reaction vessel. After then 4-5hrs dry the sample. After then to this added 50ml of 0.1N NaOH & then reflux condenser for few min in which hydrolysis is takes place. Then warm acetic acid & salicylic acid. After then untreated NaOH is titrated with standard 0.1N HCl by using phenolphthalein as indicator. Then we get calculate the acetyl salicylic acid.

$$\%\ \text{Acetyl salicylic acid} = \frac{(A-B)\ X\ n\ X\ G\ Eq\ Wt}{\text{Weight of the sample X } 100}$$

Here,

A = HCl by using blank titration

B = HCl by using sample titration

n = Normality of the sample solution

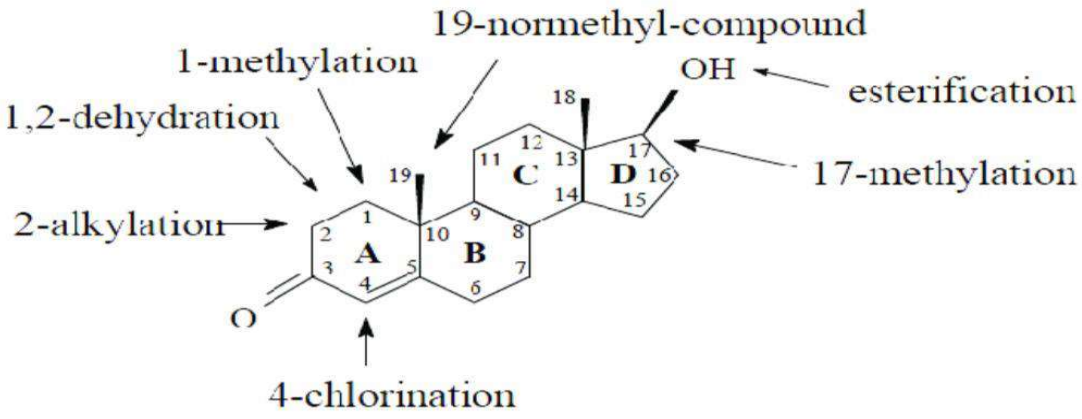
2) Testosterone, Progesterone and Cortisone (Steroids and Corticoids):-

Steroids :- (Hormones)

A steroid is a type of chemical substance found in your body, steroid can be artificially introduced in to the bodies of athletes to improve their strength. Steroids are a man made version of chemicals as hormones.

One of a large group of chemical substances classified by a specific carbon structure, steroids includes drugs used to relive swelling & inflammation, such as cortisone, vitamins- D, testosterone, and estradiol.

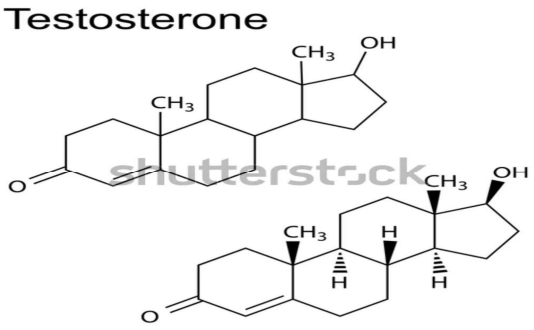
Steroid structure:-



i) Testosterone:-(Male hormone):-

It is a hormone produced by the human body. It is mainly produced in men by the testicles. The testosterone affects a man's appearance sperm production

Structure:-



Procedure:-

To take 15-20 tablets & weighed. These are powdered & also weighed. Then powder is taken in to a separating funnel & then to this added 25ml of ether & shakes the solution. Then to take aqueous layer & then it is extracted. After then the residue is taken & then to this added 0.05N Na_2CO_3. After then residue is washed with water in two times. Then it is heated, and then water & ether is evaporated. Remaining solution is taken into a 100ml volumetric flask. After then to this added alcohol. Then to take the 10ml of solution for the analysis & it is diluted to 100ml distilled water & then to take the absorbance is measured.

% Testosterone = $\frac{1000 \text{ X Cs X At X W}}{\text{N X As X A}}$

Here,

At = Absorbance of the sample
As = Absorbance of the standard solution
Cs = Concentration of standard solution
W = Initial weight of the sample
A = Weight of the powder
N = Number of tablets are taken

ii) Progesterone :-(Female hormone)

It is mainly used for the hormone disease. It is in the form of oil.

Structure:-

progesterone

Principle:-

To take the progesterone & then to this added 2, 4-DNPH & then to form a 2, 4-DNPH- Progesterone.

Procedure:-

Step-1:-

To take the required amount of the sample & after then to this added 40ml of petroleum ether standard alcohol. This is used for the dissolving purpose & then to this added few ml of 90% alcohol saturated petroleum ether. After then it is extracted into a separating funnel. Then residue is obtained to the extraction.

Step-2:-

To take above the residue & then to this added 2, 4-DNPH & then reflux for 15min & cooled, then to this added 1M HCl (or) H_2SO_4 & then reflux for 15min & cooled. Filter the solution, dried at 105^0C. After then residue is weighed &it represents the weight of the derivatives of the progesterone.

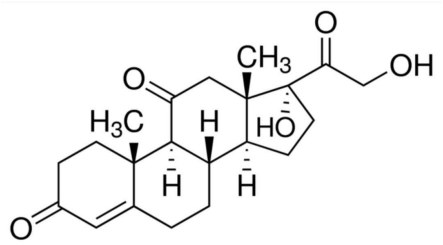
Weight of Progesterone = Weight of derivative X 0.466

% Progesterone = $\frac{\text{Weight of Progesterone}}{\text{Weight of the sample X 100}}$

Corticoids: - (Hormone)

These hormones balance stress response, energy flow, body temperature, water balance & other essential processes**.**

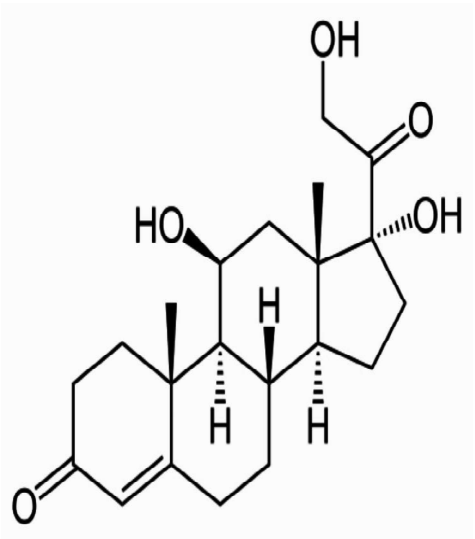
Structure:-

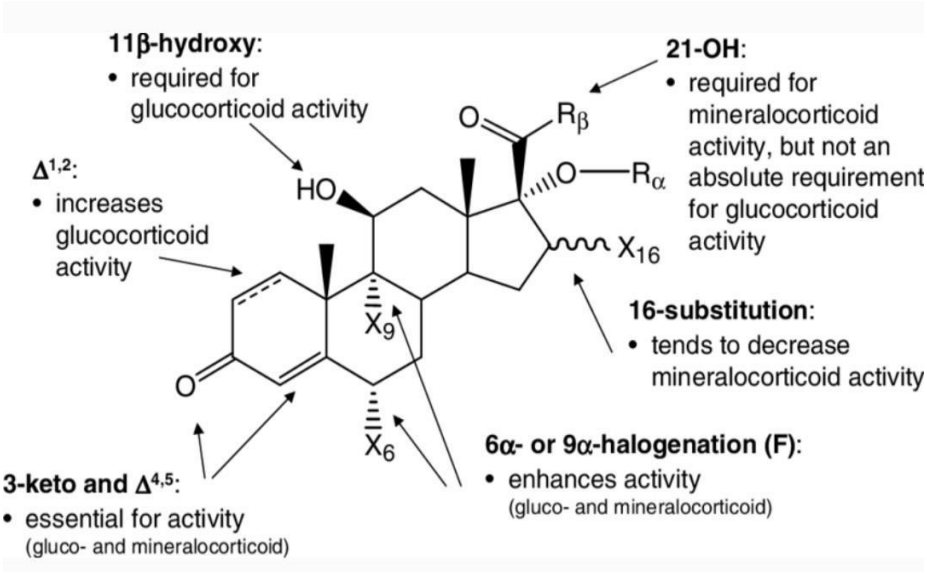


Cortisone-

It is a steroid drug. It helps decreases swelling & inflammation in your body. It works by stopping the release of molecules that causes inflammation. This also stops your body from having an immune response.

Structure:-





Principle:-

To take 17, 21 di hydroxy 20 ketone is taken, and then to this added phenyl hydrazine H_2SO_4, then to form a yellow colour complex (which is measured by using colorimetric).

Chemicals required: - diluted H_2SO_4, phenyl hydrazine H_2SO_4, standard (or) stock solution.

Procedure:-

To take two test tubes, in one test tube is taken into a 1ml of standard solution & added phenyl hydrazine H_2SO_4. After then second test tube is added 1ml of sample solution and added phenyl H_2SO_4. Then these two test tubes are kept at 60^0C in water bath & then cooled. Finally the absorbance is measured by using colorimetric method.

$$\% \text{ cortisone} = \frac{100 \times Cs \times (AI_R - AI_A)}{AS_R - AS_A}$$

Here,

Cs = Concentration of standard solution in mg/lit

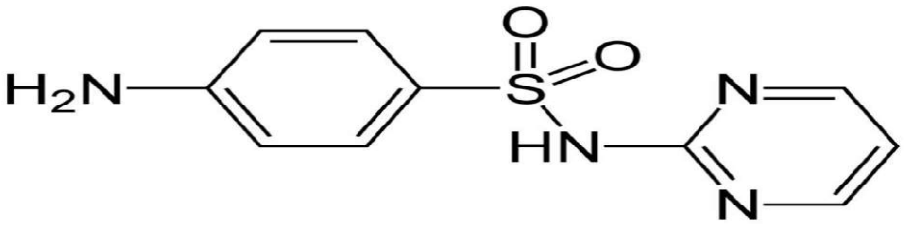
AI_R & AS_R = these are absorbance of the sample standard solution by using phenyl hydrazine H_2SO_4

AI_A & AS_A = these are absorbance of the sample standard solution by using phenyl H_2SO_4 only.

3) Sulphadiazine (Sulphadrugs):-

Synonym: - Cardiazine

Structure:-



Nucleus/derivatives: - Sulphanilamide / pyridine

Formation: - Tablets & injection

Principle:-

The sample is react with HCl & sodium nitrate ($NaNO_2$) & then to form a complex.

Chemicals required: - Standard $NaNO_2$ solution, HCl, Starch Iodine paste.

Preparation of $NaNO_2$ solution:-

Weighed out required quantity of the $NaNO_2$ & it is dissolve in water.

Procedure:-

To take 1g of sample & then to this added 40ml of concentrated HCl & 100ml of water & then this solution is heated at 25^0C & then to this added standard $NaNO_2$ solution drop wise for 4-5ml of minute. Then reaching the reaction completion take same amount of solution, this added starch iodine paste then blue colour is formed, then the reaction is completed.

$$\% \text{ Sulphadiazine} = \frac{A \times m \times \text{Molecular weight (M)}}{W \times 100}$$

Here,

A = ml of 0.1M standard $NaNO_2$ required to the sample

W = Weight of the sample

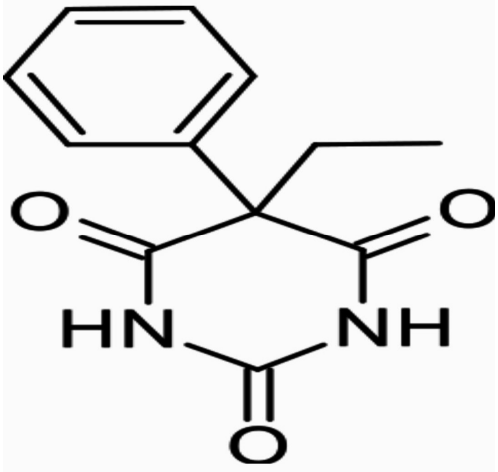
m = Morality of the sample

M = Molecular weight of the sample

4) Phenobarbitone (Barbituric acid derivatives):-

Synonym: - Luminal

Structure:-



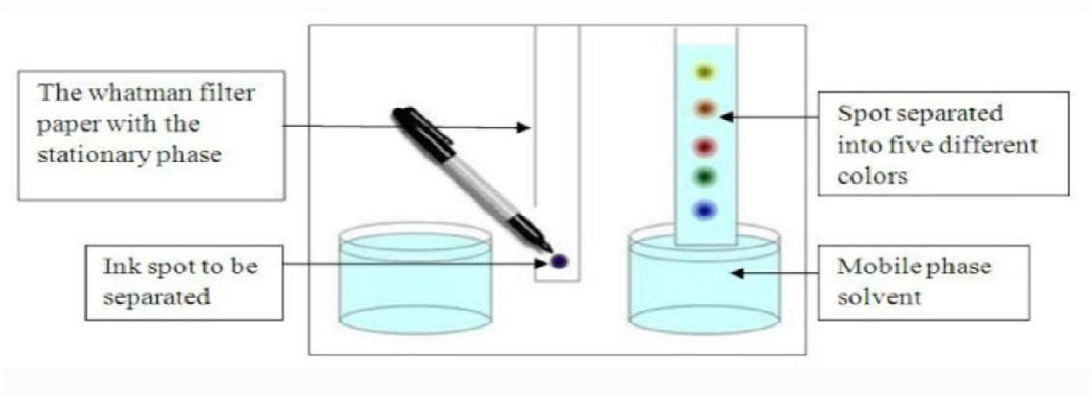
Chemical name: - 5-Ethyl, 5-Phenyl barbituric acid

Chemical required: - Acetone, Organic solvents

Principle:-

This can be determined by the using paper chromatography method.

Procedure :-(diagram)



Paper chromatography for the determination, the sample mixture is spotted & the paper by a micro syringe (or) capillary tube, then the paper is introduced into the sample solvent ethylene, solvent is do not tough the application of sample & barbitone is applied on the paper at distance from the sample.

These 2 spots are moves up wards the solvents, after reaching the solvent to $4/5^{th}$ of the paper. Then the paper is removed & then dried. Then the colour spots are observed by spraying of 0.05M $NaHCO_3$ & $AgNO_3$. After then we get black spots. Then the paper is dried & cutter.

Repeat this experiment for number of chromatographic paper & all are combining & weighed of the compound. In the place of ethylene chloride as solvent, we can use following solvents.

i) Isopropanol+$CHCl_3$+Ammonia (45:45:10)

ii) Toluene +Water +Acetic acid

Spectrophotographic/colorimetric method:-

Weighed out 10-25g of sample is dissolved in suitable solvent, which are taken into a 250ml volumetric flask, then make up to the mark with distilled water. Then filter the solution by using what man filter paper.

To take 10ml of aliquot sample solution, this is dilute to 100ml which appropriate solution. The sample solution absorbance can be measured by the calorimetrically at 270nm using blank solution. Prepare a standard solution for calibration curve. From this we known concentration we can determine the unknown.

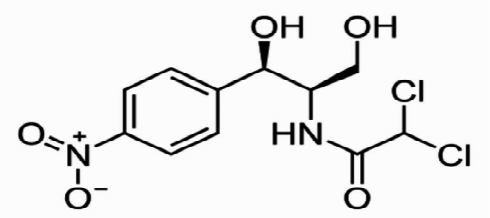
Normally barbiturate is long chain fatty acids. It can be determination of compound both in the form of tablets & capsules.

5) Chloramphenicol, Benzyl Penicillin and Tetracycline (Antibiotics):-

i) Chloramphenicol:-

Chloramphenicol is a one of the antibiotics & it is called as Chloromycetin. It is a crystalline substance obtained from the culture solution of streptomycin anigalin vagaigal. The test with a sharp melting point is one.

Structure:-



Chemical name:-$C_{11}H_{12}O_5N_2Cl_2$

Principle:-

The sample is reacted with reducing agent & then to form a colour complex. Then it is measured by spectrophotographic method.

Sample + reducing →colour complex

Chemicals required: - Sample, phosphate buffer, sodium hydro sulphate, chloroform ethyl acetate, $NaNO_2$, NEDA, NaOH, HCl

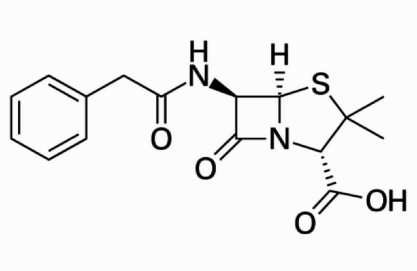
Procedure:

To take suitable weight of the sample & then it is dissolved in water & then to this added 2-5ml of phosphate buffer, then the solution containing 0.5ml of chloramphenicol. After then to this added 25ml of chloroform ethyl acetate, which is taken into a separating funnel & shake thoroughly. Then the organic & aqueous layers are separated. It is filtered through a procaine container, then the extracted residue, Then to evaporate to stream both of organic layers. Then this residue is dissolved in 3ml of 0.1N NaOH, and then added to 25ml of sodium hydro sulphate. Then this solution is stand for 15min at room temperature. Then to this added 6-10 drops of $NaNO_2$ & then 10drops of HCl is added. After 5min then to this added 1ml of 5% sulphonic acid & 2ml of NEDA is added. Then complex is formed. Then absorbance is measured by spectrophotometric method.

ii) Benzyl Penicillin: - (Penicillin G)

It is a stable in calcium salts.

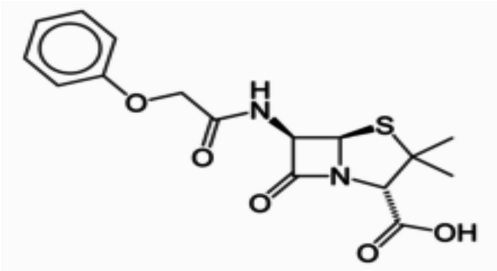
Structure:-



Test: 1:-chromo tropic acid test:-

To take required amount of sample is treated with few crystals of chromo tropic acid. Then it is dissolved in H_2SO_4. Then it is put into a glycerin bath for 2-3 hrs at 150^0C & then this solution is cooled. After then this solution is dilute with H_2SO_4.Then brown colour is observed. It is identification of Penicillin-G. When the colour is deep blue (or) purple then it is Penicillin -V.

Structure of penicillin -V:-

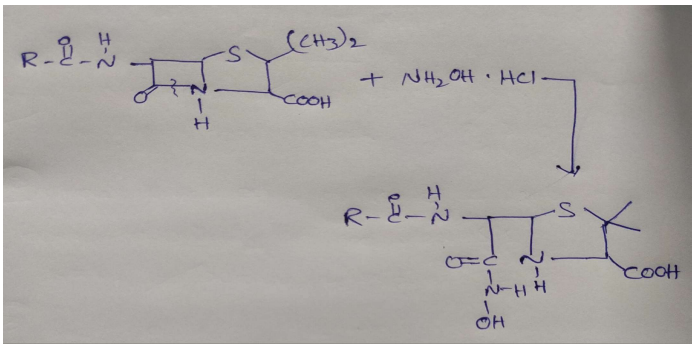


Test: 2:-fluorescence test:-

Determination of $NH_2OH.HCl$ test:-

Principle:-

Sample + $NH_2OH.HCl$→complex

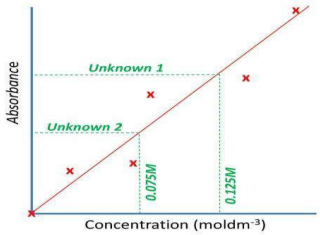


Chemicals required: - Sample, $NH_2OH.HCl$, Buffer (NaOH CH_3COONa), ferric ammonium sulphate

Procedure:-

When the sample is treated with $NH_2OH.HCl$ & it is allow to stand for 5min & then to this added 1ml of buffer & few ml of ammonium sulphate & shake thoroughly & then this solution is stand for 5min & then we can observe colour from spectrographic method, then we can calculate the titrate with blank solution.

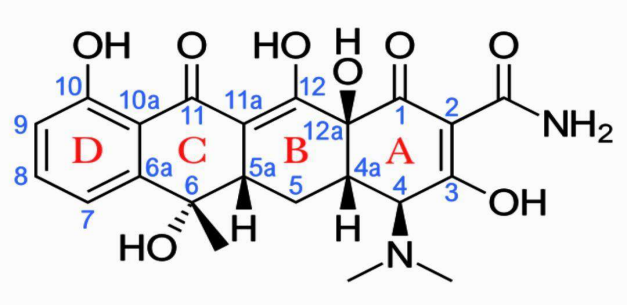
Graph:-



iii) Tetracycline:-

It is an antibiotics, these is a free base, which is insoluble in water, these form derivative with HCl.

Structure:-



H_2SO_4 test:-

To take 1mg of sample & after then to this added 1ml of H_2SO_4. Then this solution is shaking for 2sec & then observes the colour. It produces a deep violet colour-tetracycline.

Oxy tetra cycline produces red colour, chloro tetracycline produces-deep blue to green colour.

Fluorescence test:-

To take 10-15mg of sample & after then to mix the 1ml of 2N NaOH. After then absorb the fluorescence.

Note:-

Firstly the sample is dissolved in water.

Tetracycline-orange –yellow -blue.

To take 2ml of concentrated HCl is added to the sample.

Oxy tetracycline-green fluorescence

Fluoro tetracycline - no fluorescence.

Spectrophotographic method (or) $FeCl_3$ method:-

$FeCl_3$ is added to the tetracycline & then to produce an orange brown colour.

Preparation of $FeCl_3$ solution:-

500mg of $FeCl_3$ is dissolved 0.01N HCl solution in one liter solution.

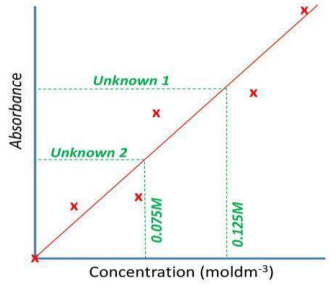
Preparation of tetracycline solution:-

1g of tetracycline is dissolved in 0.01N HCl solution.

Procedure:-

To take 5ml of aliquots sample & then to this added 5ml of water in 50ml of volumetric flask & then to this added 10ml of $FeCl_3$ solution, then dilute to 50ml & we take, after then it is kept for 10min a side. Then orange colour is observed. Then it is absorbance is measure at 470nm. Then we get a standard curve. It is in the form of tablets & injections. It is cure for the typhoid, malaria and other fevers etc...

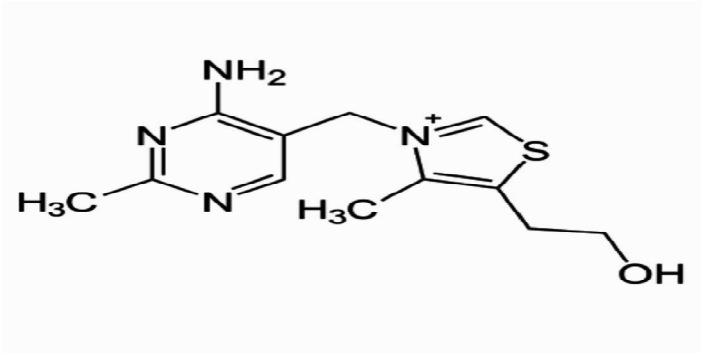
Graph:-



6) Thiamine (B1), Riboflavin (B2) and Ascorbic acid(C) [Vitamins]:-

i) Thiamine (B1):-

Structure:-



Principle:-

The sample is reacted with 6-amino thiamine then to form a complex.

Chemicals required: - 0.1N $NaNO_2$, 20% NaOH, mixture solvent (90ml toluene+10ml n-butanol), 6-amino thiamine.

Procedure:-

Step: 1:-

Weighed out 20 tablets of sample & then these tablets are powdered & then weighed. Then to this added mixture solvent & 60ml of HCl is added. Then dissolve the powder. Then the solution is shaking for one hour. Then it is filter & then precipitate is washed several times with $HCl+H_2O$ mixtures. After then washing & diluting 100ml.

To take 10ml of sample solution from the above solution and make up to 100ml with water & this is used for the sample.

Step: 2:-

To take the 5ml of 6-amino thiamine solution. This solution is cooled in ice bath to 0^0C & then to this added $NaNO_2$ Of 2ml & this solution is stand for few min. after then to this added 5ml of 20% NaOH solution, dilute to 20ml solution. To take 1ml of reagent solution & then to this added 1ml of sample solution is taken into a graduated flask & then kept for 5min,then colour is observed. Then its absorbance is measured by using colorimetric method.

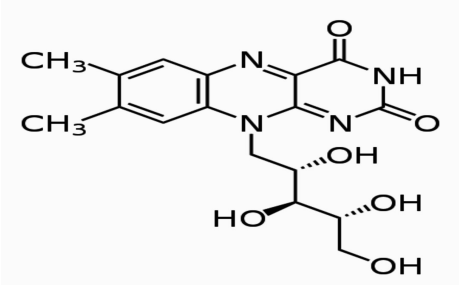
$$\text{Thiamine mg /ml} = As/A_R \text{ mg/ml}$$

As= Absorbance of the sample solution

A_R= Absorbance of the standard solution

ii) Riboflavin (B2):-

Structure:-



It is yellow (or) orange yellow colour. The melting point is 282^0C.

It is less soluble in water; it is soluble in alcoholic solvent.

The important property is fluorescence in riboflavin. It exhibits yellow green fluorescence at 565nm, pH-6 under UV light.

It shows maximum absorbance 267nm, it is shows maximum sample. It is stable in minerals acids & sensitive in alcoholics.

The following methods are:

1) Fluoro metric method

2) Spectrometric method

3) Coloro graphic method

Spectrometric method:-

Step: 1:-

Weighed out 20mg of riboflavin is taken into a RBF. Then to this added water in it is not soluble. After then to this added 5ml of 1N NaOH. Then the sample is dissolved. After then to this added 2ml of 5N CH_3COOH, then the solution is making up with water to one liter flask.

Step: 2:-

The above solution is used for the analysis from this we take 20ml of sample solution & then to this added 25ml of $CHCl_3$. These are taken into a separating funnel & shake thoroughly for 1-2min, then the extract aqueous layer. Then added again 25ml of $CHCl_3$ & shake & extract aqueous layer. Then discard the organic layer, Then to measure the absorbance & then again to measure the blank solution.

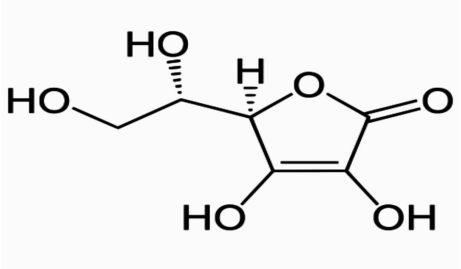
$$\% \text{ Riboflavin (B2)} = 100 \text{ X } \frac{\text{As X Wr}}{\text{Ar X } w_S}$$

Here,

As = Absorbance of the sample solution
Ar = Absorbance of the standard solution
w_S = Weight of the sample solution
Wr = Weight of the standard solution

iii) Ascorbic acid(C):-

Structure:-



It is obtained white (or) yellow crystalline (or) powder form. When it is exposed to air then oxidation takes place & then to form de hydro ascorbic acid.

Determination of ascorbic acid by using 4-methoxy-2-nitro-aniline:-

Principle:-

The ascorbic acid is reacted with 4-methoxy-2-nitro-aniline to form a deep blue colour complex. The absorbance is measure by spectrophotographic method.

Preparation of reagents:-

Amino reagent:-

To take 126ml of glacial acetic acid & add to 500mg of recrystalized 4-methoxy-2-nitro-aniline. After dissolving it is dissolved in 250ml.

Ascorbic stock solution:-

Standard sample dissolved in 0.5% of oxalic acid & the final concentration is 0.5mg/ml.

Standard 'A':-

A dilution containing 1mg of ascorbic acid must be prepared in stock solution.

Standard 'B':-

A dilution containing 1.5mg of ascorbic acid must be prepared in stock solution.

Procedure:-

To take 2ml of amino reagent in 250ml glass stopped bottle. After then to this added 2ml of $NaNO_2$ solution then orange colour (foots) & shaking the solution until disappearing of the colour and then to this added 75ml of N-butanol is added & shake thoroughly after then to this added sample in which 0.5-2mg concentration of ascorbic acid. After then thoroughly mixed for several min. filter the precipitate & transfer it to 500ml separating funnel and then to this added 25ml of 10% of NaOH solution followed by 150ml ether. Shake the content & separate the layers. Aqueous layer is transfer to 200ml of volumetric flask. The organic layer is extracted with 10% NaOH (3times), then again filter (3times) aqueous layer & transfer it to before collected aqueous layer & then make up 200ml & shake this sample solution. Blank sample is also prepared without adding amino acids. Standard 'A', standard 'B', sample blank are determined by same procedure & absorbance of at 570nm.

Ascorbic acid in aliquot sample solution = $\frac{W_A + (W_B - W_A) + (A_S - A_A)}{A_B - A_A}$

7) Isoniazid (Anti micro bacterial agents):-

Antibacterial are used to treat bacterial infections.

Isoniazid is an antibiotic that fights bacteria. Isoniazid is used to treat and to prevent tuberculosis (TB).

Isoniazid is in a class of medications called anti tuberculosis agents. It works by killing the bacteria that cause tuberculosis.

First synthesis was described in 1912. A. Kachugin invented the drug against tuberculosis under name Tubazid in 1926. It is synthesized in the early 20th century. Isoniazid is available in tablet, syrup and injects able forms. To take the over dosage and otherwise the symptoms are Vomiting, dizziness, respiratory distress.

Synonym:-Nydrazide

Structure:-

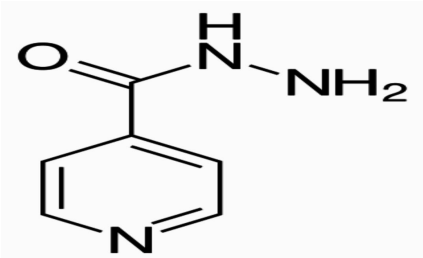
Chemical name: - Isonicotinic hydrazide

Nucleus/derivatives: - Pyridine, hydrazide of isonicotinic acid.

Formula: -$C_6H_7N_3O$

Melting point: -171.4 °C

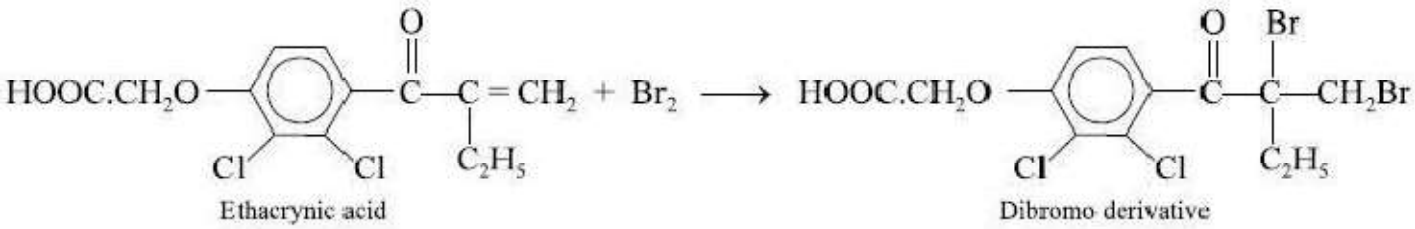
Structure:-



Principle:-

The sample is reacted with brominating mixture, then to form bromine substituted isoniazid. Then the untreated bromine is treated with KI. After then iodine is liberated, then liberated iodine is titrated with standard hypo by using starch as an indicator.

$$KBrO_3 + 5KBr + 6HCl \longrightarrow 6Br^{\ominus} + 6KCl + 3H_2O$$



Procedure:-

To take 0.4g of sample is taken into a reaction vessel, it is dissolved in acetic acid, after then to this added 20m of bromine in HCl & mix, the connect allow to stand for one hour in dark place & then to this added 100ml of water & 20ml of KI and this solution is shake thoroughly, then iodine is liberated, the liberated iodine is titrated with standard hypo by using starch as a indicator, then it is determined by the weight of isoniazid present in the given sample.

Factor: - 1ml of 0.1N Br_2 = 0.003429g of isoniazid

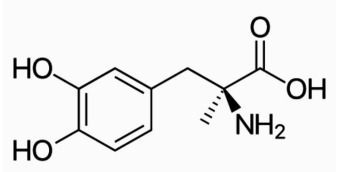
8) Methyldopa (Antihypertensive agents):-

Antihypertensive are a class of drugs that are used to treat hypertension (high blood pressure).This therapy seeks to prevent the complications of high blood pressure, such as stroke and myocardial infarction.

Methyldopa is used to treat high blood pressure. Methyldopa is in a class of medications called antihypertensive. It works by relaxing the blood vessels so that blood can flow more easily through the body. It is introduction in 1960.

Synonym: - Aldomet

Structure:-



Chemical name: - 3, 3, 4 di hydroxy phenyl-2-methyl alanine

Nucleus/derivatives: - Alanine & hydroxyl phenyl group

Structure contains: - Carboxylic acid group (COOH), amino acid group, primary amines, ketacal group

Principle:-

The sample is treated with acetylating mixture. i.e.; acetic anhydride & pyridine to form R-NH-$COCH_3$ & CH_3COOH, This acetic acid is titrated with standard NaOH by using phenolphthalein.

Chemicals required: - acetic anhydride, NaOH, pyridine, sample, and phenolphthalein

Procedure:-

To take 0.2-0.5g of sample is taken into a conical flask, then to this added 10-20ml of acetylating mixture. Then it is reflux for few min in water bath, then to form a acetic acid, the acid is titrated with standard NaOH by using phenolphthalein finally colour change & then we get a end point.

$$\text{Weight of the Methyldopa} = \frac{(V_1 - V^2) \times N \times G \text{ Eq Wt}}{1000}$$

$$\% \text{ Methyldopa} = \frac{\text{Weight of methyldopa}}{\text{Weight of the sample}} \times 100$$

Here,

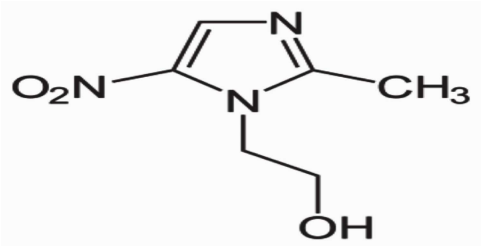
V_1 = Volume of NaOH during the blank titration
V2= Volume of NaOH during the sample titration
N = Normality of NaOH

9) Metronidazole (Ant amoebic agents):-

Metronidazole is an antibiotic that is used to treat a wide variety of infections. It works by stopping the growth of certain bacteria and parasites. It is used either alone or with other antibiotics to treat pelvic inflammatory disease.

Synonym:-Flagyl

Structure:-



Chemical name: - 2-(2-methyl 5-nitro imidazole-y[l])-ethanol

Nucleus/derivatives: - Imidazole/ethanol group

Chemicals required: - Sample, $TiCl_3$, HF, HCl, NH_4SCN, ferric alum

Principle:-

$$R\text{-}NO_2+6[H] + H^+ \rightarrow R\text{-}NH_2+H_2O$$

Procedure:-

Required quantity of sample is taken into a RBF & it is dissolve in water & then to pass N_2 gas to free from O_2. After maintaining inert atmosphere & then added known excess of $TiCl_3$ & 30ml of HCl & 2ml of HF. These solution condense boil up to 5-8min, then cool the solution, then it is titrates with ferric alum by using NH_4SCN as indicator.

$$\text{Weight of the metronidazole} = \frac{(V\text{-}C)\ X\ M}{1000\ X\ A}$$

Here,

V = Volume of ferric alum during the blank titration
C= Volume of ferric alum during the sample titration
M = Molecular weight of the sample
A = Number of hydrogen required for process.