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Module No.	:	03
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Learning Outcome of Module-3

LO	Learning Outcome (LO)	Course Outcome Code
LO1	To gain knowledge about Precipitation Titration	BP102.3
LO2	To understand the methods of precipitation Titration	BP102.3
LO3	To gain knowledge Complexes, Ligands, Chelates and Classification	BP102.3
LO4	To understand Masking and Demasking agents, Metal ion indicators.	BP102.3
LO5	To gain knowledge about concept and techniques of oxidation and reduction.	BP102.3
LO6	To gain knowledge about Diazotisation reaction and techniques of diazonium salt formation	BP102.3

Module Content Table

Topic
• Precipitation titrations: Mohr's method, • Volhard's, • Modified Volhard's • Fajans method, • estimation of sodium chloride. • Classification of Complexometric titration • Metal ion indicator, Making and Demasking agent • Estimation of Magnesium Sulphate and Calcioum gluconate • Gravimetry Principle • Steps involved in the Gravimetry • Estimation of Barium sulphate • Principle, Procedure and Types and Applications of Diazotisation

PRECIPITATION TITRATIONS

A **titration** is an analytical procedure in which a reagent called a **titrant** is slowly added to another substance. A rapid stoichiometric reaction takes place as the titrant is added, and both the addition and the reaction continue until one of the reactants is exhausted. Some process, device, or change in the solution indicates that this endpoint has been reached. The purpose of a titration is to determine the amount, or the concentration, of one of the reactants, which can be done if the amount, or concentration and volume, of the other reactant required reaching the endpoint of the titration is known.

In a precipitation titration, the stoichiometric reaction is a reaction which produces in solution a slightly soluble salt that precipitates out. To determine the concentration of chloride ion in a particular solution, one could titrate this solution with a solution of a silver salt, say silver nitrate, whose concentration is known. The chemical reaction occurring is

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s).$$

A white precipitate of AgCl is deposited on the bottom of the flask during the course of the titration. Since the chemical reaction is one silver ion to one chloride ion, we know that the amount of silver ion used to the equivalence point equals the amount of chloride ion originally present. Since by the definition of molarity $n = cV$, the number of moles of either silver ion or chloride ion can be calculated from the number of moles of the other, and the molar concentration or the volume of added solution can be calculated for either ion if the other is known.

Example. In a precipitation titration of 46.00 mL of a chloride solution of unknown concentration, 31.00 mL of 0.6973 molar $AgNO_3$ were required to reach the equivalence point. The molar concentration of the unknown solution is calculated as follows:

$$31.00 \text{ mL} \times 0.6973 \text{ molar} = 21.62 \text{ mmol } Ag^+ = 21.62 \text{ mmol } Cl^-$$

$$21.62 \text{ mmol } Cl^-/46.00 \text{ mL } Cl^- = 0.4700 \text{ molar } Cl^-$$

The substance to be titrated is generally measured into the titration vessel either directly, its mass (or density and volume) having been determined, or by **pipette** if it is in the form of a solution. The titrant solution is generally delivered from a **burette**. The volume added can be measured from the burette scale as soon as the endpoint of the titration is reached.

p Notation

It is inconvenient to the point of being impractical to plot, or even to compare, the changes in ionic concentrations which take place over the course of a precipitation titration because the values of the concentrations cover so many orders of magnitude in range. Chemists have therefore introduced p notation, in which the negative logarithm of a concentration or activity is used rather than the concentration or activity itself; that is, pX = -log *c*(X) or pX = -log *a*(X). The logarithmic p notation is commonly used not only in titrations but for the general expression of solution concentrations. In other sections this notation, in the form of pH, is extensively used to express the acidity of solutions.

The molar concentration of either chloride ion or silver ion will change over several orders of magnitude during the course of a titration, as the concentration of chloride ion is first slowly reduced by the precipitation of AgCl as a consequence of the continuous addition of silver ion. As the supply of chloride ion is reduced to very low values, the equivalence point of the titration is reached--the point at which the stoichiometric precipitation is complete and the amount of silver ion that has been added is equivalent to the amount of chloride ion originally present. The term "equivalent" is used rather than "equal" because in some reactions, such as the precipitation of Ag_2SO_4, the amounts will differ by a stoichiometric factor of two or three. Beyond the equivalence point, addition of more silver ion will continue to reduce the concentration of chloride ion through the common ion effect.

End points

In any titration, it is necessary to have some method of detecting when just enough of the titrant has been added -- a procedure known as detecting the endpoint of the titration. The endpoint of this titration can be detected if the rapid change in either the concentration of silver ion or the the concentration of chloride ion which occurs at the endpoint can be made apparent to an observer. Either instrumental methods or equilibrium methods can be used. The equilibrium methods are fairly straightforward. In this case we can use Ag_2CrO_4, because a solution of CrO_4^{2-} is yellow while a solution or precipitate of Ag_2CrO_4 is blood-red.

Suppose $[CrO_4^{2-}]$ in the solution is 0.001 molar. Then $K_{sp} = 1.12 \times 10^{-12} = [Ag^+]^2[CrO_4^{2-}]$. Since $[CrO_4^{2-}] = 10^{-3}$ molar, $[Ag^+]^2 = 1.12 \times 10^{-10}$, and $[Ag^+] = 3.35 \times 10^{-5}$. At any concentration of silver ion greater than 3.35×10^{-5} molar in such a solution, a precipitate of Ag_2CrO_4 will form. If the concentration is below this, no silver chromate precipitate will form.

When we have a solution of, say, 0.01 molar chloride ion and add silver ion to it, the solubility product is K_{sp} = 1.76 x 10^{-10} = [Ag^+][Cl^-], so at the start of the titration [Ag^+] = 1.76 x 10^{-10}/1 x 10^{-2} = 1.76 x 10^{-8} and no precipitate of Ag_2CrO_4 can form. At the equivalence point, [Ag^+] = [Cl^-] and [Ag^+]^2 = [K_{sp}] = 1.76 x 10^{-1}, [Ag^+] = 1.33 x 10^{-5} and no precipitate will form. But when a drop or two more of silver nitrate solution is added after the equivalence point has been reached, there is no more chloride ion to react with it. The concentration of silver ion may go up to say 10^{-3} molar. The solubility product of silver chromate will then be exceeded and a red precipitate of Ag_2CrO_4 will designate the end of the titration. This is known as the **Mohr method** of chloride determination.

A reaction in which the analyte and titrant form an insoluble precipitate also can serve as the basis for a titration. We call this type of titration a **precipitation titration**. One of the earliest precipitation titrations—developed at the end of the eighteenth century—was the analysis of K_2CO_3 and K_2SO_4 in potash. Calcium nitrate, $Ca(NO_3)_2$, was used as the titrant, forming a precipitate of $CaCO_3$ and $CaSO_4$. The titration's end point was signaled by noting when the addition of titrant ceased to generate additional precipitate. The importance of precipitation titrimetry as an analytical method reached its zenith in the nineteenth century when several methods were developed for determining Ag^+ and halide ions.

The precipitation titrations are those in which a chemical reaction results in the formation of a precipitate or a sparingly soluble salt. Such titrations are not as numerous as redox or acid-base titrations. In fact the most popular of these titrations are usually limited to those involving the precipitation Ag^+ ion with anions like halogens or thiocyanate (SCN^-). One of the main reasons for the limited use of such titrations is lack of suitable indicators to detect the end point. The other reasons are the slow rate of reaction in such a titration. As the end point is approached, the titrant is added slowly, a high degree of supersaturation does not exist and the rate of precipitation may be too slow. Furthermore, the composition of the precipitate may not be exactly known owing to coprecipitation effects. Thus the main precipitation titrations are the argentometric titrations which employ a standard solution of silver nitrate. Even in argentometric titrations which will be considered here, strictly speaking, complex formation reaction is involved rather than precipitation reaction.

When $AgNO_3$ is added to a solution of NaCl/ KCl or KSCN/ NH_4SCN, a white precipitate of either AgCl or AgSCN is formed:

$$AgNO_3 + NaCl \longrightarrow \downarrow AgCl + NaNO_3$$

$$AgNO_3 + KSCN \longrightarrow \downarrow AgSCN + KNO_3$$

Both these reactions may be employed for the titrimetric determination of Ag^+, halide or SCN^- (thiocyanate) ions. Since both the solutions of NaCl and KSCN are colourless, the end points in both the cases can only be ascertained with the help of an indicator.

In neutral solution of NaCl and $AgNO_3$ (Mohr's method), potassium chromate (K_2CrO_4) solution is used as an indicator, whereas, in silver nitrate and KSCN (Volhard's method) an acidic solution of ferric alum is used as an indicator. A slight excess of a thiocyanate solution produces a blood red colour with ferric alum. Likewise in Mohr's method, a slight excess of Ag^+ ions produce a red colour with K_2CrO_4, due to the formation of Ag_2CrO_4 (brick red).

Potassium chromate can only be used in neutral solution since, i) Ag_2CrO_4 dissolves in acids ii) an alkaline solution would react with silver nitrate to form a precipitate of silver oxide:

$$2AgNO_3 + 2NaOH \longrightarrow Ag_2O + H_2O + 2NaNO_3$$

Nevertheless, an acidic solution of a chloride can be determined by Mohr's method, by first neutralizing it with $CaCO_3$. It is because of such shortcomings of Mohr's method, that Volhard's method is preferred, since in the latter method, determination can be carried out even in the presence of free mineral acid. A second disadvantage is that the Mohr's method is not satisfactory for the determination of iodides.

The adsorption of a coloured organic compound (Fajan's Adsorption indicators) on the surface of a precipitate may induce electronic shifts in the molecule which changes its colour. Such a phenomenon of colour change may be used to detect the end point of precipitation titrations of silver salts. Thus when $AgNO_3$ is added to NaCl containing an adsorption indicator (e.g. fluorescein) the colour at the end point changes from light yellow to rose pink. On standing, the precipitate appears coloured pink or red, while the solution becomes colourless due to adsorption of indicator on the AgCl precipitate. It may be noted that the colour of a substance is modified by adsorption on a surface. The reaction of an anionic indicator such as fluorescein may be exhibited as:

Let the indicator is shown as Fl^- - fluorescein $C_{20}H_{11}O_5$

If excess Cl: (AgCl) $Cl^- + Fl^- \longrightarrow$ no reaction

If excess Cl: (AgCl) $Ag^+ + Fl^- \longrightarrow$ (AgCl) (AgFl) adsorbed

In the case of a cationic indicator (let it be IN^+) the reactions is:

If excess Cl: (AgCl) $Cl^- + IN^+ \longrightarrow$ (AgCl) (Cl^-IN^+) adsorption

If excess Cl: (AgCl) $Ag^+ + IN^+ \longrightarrow$ no reaction

The example of a cationic indicator, IN^+ is methyl violet.

Factors Affecting Solubility of the Precipitate

Common ion effect on solubility (C.I.): A common ion is one of the component ions of sparingly soluble salt but found in solution from ionization of other salts e.g. if AgCl is dissolved in NaCl or KC1. The chloride ion obtained from ionization of these salts form a common ion with chloride ion produced from ionization of AgCl, similarly if AgCl is dissolved in AgN03 solution. The common ion usually causes depression of the solubility. Thus, if we have a saturated solution of sparingly soluble salt e.g. AgCl there is equilibrium between solid phase and soluble molecule i.e. with the ions in solution. To illustrate the C.I. effect we will discuss the case when Cl− or Ag+ are added to saturated solution of AgCl. Thus, if AgCl(S) is shaken with pure water SpAgCl = [Ag+] [Cl−], if Ag+ are added (from AgNO3) excess Ag+ will disturb the equilibrium and this ions will combine with Cl− to form precipitate AgCl till equilibrium is again reached where [Ag+] [Cl−] = SpAgCl i.e. the solubility decreases. A similar effect occurs if excess Cl− is added to the solution. One can calculate the extent of the depression of the solubility if the concentration of common ion is known.

Example: Calculate the solubilities of AgCl in 0.001 M, 0.01M and 0.1M KC1.

In 0.001 M KC1 $[Cl^-] = 10^{-3}$

In a saturated solution of AgCl $SpAgCl = [Ag^+]\,[Cl^-]$ $1.1 \times l0^{-10}$

$$= [Ag^+][10^{-3}]$$

$$10^{-7} \approx [Ag^+]$$

$\therefore$ molar solubility of $AgCl = 10^{-7}$

This is explained by the that fact Ag+ is found in solution only from the ionization of soluble part of AgCl at saturation, and since each 1 molar Ag+ concentration = [AgCl] $\therefore$ mol AgCl furnishes one Ag+ soluble.

Similarly in 0.01 M KC1 solution $[Cl^-] = 10^{-2}$

$1.1 \times l0^{-10} = [Ag^+][10^{-2}]$

$[Ag] = 10^{-8}$

molar solubility of [AgCl] = 10^{-9} in 0.1 KC1 solution the solubility will be 10^{-9} In pure water 1.05×10^{-5} S= SpAgCl

Depression of solubility by common ion effect is of great importance in gravimetric analysis, to ensure complete precipitation excess of precipitating agent is added which by common ion effect

minimize the solubility. However, in some cases the presence of common ion may increase solubility and this is due to complex formation and must be avoided.

Increased solubility by complex formation: The solubility can be increased by including an ion which forms a complex with one of ion components of the precipitate, e.g. when potassium cyanide is added to silver nitrate a white precipitate of silver cyanide is first formed, because the solubility product of silver cyanide is exceeded. Addition of excess CN^- will dissolve the precipitate due to the formation of complex ion $[Ag(CN)_2]^-$.

Notice that AgCl, AgBr and Agl are soluble in alkaline cyanide solutions while Ag2S is not (SpAg2s =10^{-51}). Also silver ion forms complex with ammonia.

$Ag+ + 2NH_3 \rightarrow [Ag(NH_3)_2]+$

The concentration of silver ion produced from dissociation of the complex is insufficient in presence of chloride to exceed the solubility product of silver chloride but it approaches that of bromide and exceeds that of iodide in their presence. So silver chloride is soluble in ammonia while bromide is partially soluble and silver iodide is insoluble.

Effect of temperature on solubility: Increase of temperature mostly increases the solubility of precipitate.

Diverse ion effect: Diverse salts increase the solubility of precipitates and have more effect on precipitates with multiply charged ions.

The presence of diverse salts will generally increase the solubility of precipitates due to the shielding of the dissociated ionic species, for example $BaSO_4$ in presence of $NaNO_3$ (diverse ion).

Effect of solvent: The solubility of most inorganic compounds is reduced by the addition of organic solvents such as methanol, ethanol, propan-1-ol and acetone. For example, the addition of about 20 vol% ethanol renders the solubility of lead sulphate practically negligible, thus permitting quantitative separation. Similarly, calcium sulphate separates quantitatively from 50 vol% ethanol.

Fractional Precipitation

When a precipitating agent such as Ag+ is added to a solution containing two anions e.g. chloride and iodide both of which form slightly soluble salt with the same cation. The solubility product of AgCl and Agl is $l.lxl0^{-10}$ and $1.7x10^{-16}$ respectively.

Preparation of their 0.1N Standard Solutions

Silver Nitrate: This is the only silver salt official in IP. This is the most important silver salt. It is usually prepared by dissolving Ag in hot dilute HNO_3 in a porcelain or stainless steel vessel. The resulting solution is evaporated to crystallization. The crystals obtained are purified by recrystallisation from distilled water (chloride free).

$$3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + 2H_2O + NO \uparrow$$

It forms colourless transparent rhombic crystals of density 4.35 and m.p. 212ºC. It can also be casted into sticks (called lunar caustic) and has a strong caustic action. It burns skin which sustains black colour after it is touched. It is highly soluble in water and the solubility increases with rise of temperature. It is also soluble in alcohol and pyridine. It also exists as a white powder; it is odourless and has a bitter metallic taste. Pharmacopoeial quality must be more than 99.5% pure. The pH of a 4% w/v solution is 5.4-6.4. The solution slowly darkens if exposed to light.

It is relatively non-toxic, even when taken internally since it reacts with proteins forming non-toxic complexes. It is poorly absorbed from the gastrointestinal tract. It is astringent and caustic. The caustic property is utilized to destroy warts and corns etc. It is used as 1% w/v solution for local antibacterial action. It is applied to burns to reduce infections. It is used in eye drops where it functions both as a prophylactic and in the treatment of infection. Eye drops are rendered isotonic with added $NaNO_3$. Sometimes toughened silver nitrate, containing 5% w/w of KNO_3 is used in place of $AgNO_3$. To reduce caustic and astringent properties, silver proteinate is used in place of silver nitrate. Ammonical silver nitrate is used in dental practice. This is prepared by dissolving the first precipitated silver oxide in excess of ammonia, whereby a soluble complex salt, $[Ag(NH_3)_2](OH)$ is formed. This solution is used for application in dental crevices where, later on metallic Ag by reduction is precipitated to fill the crevices.

Limits are prescribed for bismuth, copper, lead, foreign substances, clarity and colour of 1% w/v solution.

Silver nitrate and its solutions are stored in well closed dark coloured bottles and out of light.

Standard 0.1N $AgNO_3$ solution: AR $AgNO_3$ has a purity of atleast 99.9% nd hence a standard solution can be prepared by direct weighing. AR $AgNO_3$ is dried at 120ºC for 2 hours and allowed to cool in a small closed container in desiccators. The relationship among equivalents of $AgNO_3$, KCl , NaCl, NH_4SCN and KSCN exists as:

$AgNO_3$ = KCl = NaCl = NH_4SCN = KSCN

169.9 74.5 58.45 76.0 97.2

Weigh out accurately 8.494 g of AR $AgNO_3$ (dry) or pure recrystallised material and dissolve it in chloride free water and make upto 500 cm^3 in a graduated flask. This gives a 0.1 N or 0.1 M solution. The solution should be stored in an amber-coloured glass bottle and protected from light.

Sodium chloride: NaCl is very widely distributed in nature. It is the electrolyte of most extracellular body fluids. Sea water contains 2.5-3.0% NaCl.

Sea water is run into the outer deepest pan and allowed to evaporate in sun and wind until it gains the consistency of brine. It is then passed to other pans of gradually increasing shallowness and the evaporation is continued until the salt crystallizes out. The crystals are collected in heaps and washed with water or by means of rain to remove highly soluble magnesium chloride and finally sieved to collect the fine variety of salts. The brine having minor impurities is diluted with water and saturated with HCl gas, doing so throws out pure NaCl, the impurities are left behind in the solution. NaCl is extensively used in making parenteral solution, as the commonest vehicle for the administration of other drugs into the body system; hence it should be highly pure.

NaCl forms colourless, odourless crystals with a characteristic salty taste. It is freely soluble in water, soluble in glycerol and slightly in alcohol. Heat does not appreciably increase either the rate of dissolution or the solubility itself. An aqueous solution (0.9% w/v of NaCl) is isoosmotic with blood serum and other body fluids. Such a solution is also called as isotonic or physiological or normal saline. Each 1g of NaCl represents 17.1 millimoles of sodium and 17.1 millimoles of chloride. The pharmacopoeia includes several solutions containing NaCl as the major ingredient.

For medicinal purposes domestic common salt, rock salt and table salts are not used since these contain externally added substances to reduce caking, improve free flowing and sometimes added iodides and fluorides to correct for dietary deficiencies.

NaCl, IP, should be free from acidic and alkaline impurities, arsenic, iron, heavy metals, Ca, Mg, Ba, iodides, bromides, sulphates and $Na_4[Fe(CN)_6]$. Some of these are natural impurities whereas others (e.g. Ba and ferrocyanide) added for purification. The moisture content as checked by the requirement of loss on drying should not exceed 1% w/w dried at 130ºC. NaCl intended for parenteral administration should not contain more than 0.1% w/w of potassium.

It is stored in well closed containers to prevent absorption of moisture.

Standard 0.1 N NaCl solutions: Pure and dry analytical grade reagent NaCl may be weighed accurately about 5.85 g per dm^3 of solution and dissolve in a one dm^3 graduated flask in chloride free water (0.1 N). If this is to be used as an intermediate solution 5.85 g of pure and dry AR NaCl dissolved in a 1 dm^3 graduated cylinder and standardize it against standard 0.1 N $AgNO_3$ solution by the methods to be shortly described.

Sodium chloride injection, IP: It is a 0.9% w/v solution employed for intravenous infusion as vehicle for other chemicals or for replenishing fluids or electrolytes. It has 150 millimoles of sodium and chloride ions per dm^3.

Sodium chloride hypertonic injection, IP: It is a 1.6% w/v solution (1.52-1.68% w/v) and is used for replenishing fluids and electrolytes. It has a lower limit for As (0.2ppm) than for NaCl itself.

Compound NaCl injection, IP: It is also called Ringer's solution and contains 0.86% w/v of NaCl, 0.03% w/v of KCl and 0.033% w/v of calcium chloride and is used for replenishing electrolytes and as a fluid. In addition to limits for NaCl, the injections are tested for the total absence of pyrogens. One form of Ringer's solution has the same composition but is employed for external use for irrigation of wounds and broken surfaces of the body. All the solutions are sterilized by filtration or in a furnace.

Sodium chloride and dextrose injection, IP: These are used as nutrient, fluid and electrolyte replenisher by intravenous infusion; supplied in 0.11% w/v-0.9% w/v of NaCl and 2.5-25% w/v of dextrose in water for injection.

Potassium Chloride: KCl, IP, is obtained by separation, purification and crystallization from the minerals, carnallite, $KCl.MgCl_2.6H_2O$ or from sylvine. On a laboratory scale it can be prepared by neutralizing potash ash (K_2CO_3) with dilute HCl.

It is a colourless, odourless crystalline solid with a salty taste. It is freely soluble in water, soluble in glycerol and sparingly soluble in alcohol and insoluble in absolute alcohol and ether. It has m.p. 786ºC and b.p. 1411ºC. It resembles NaCl closely except that its solubility increases rapidly with the temperature and is more readily fusible. A 1.19% w/v solution is isoosmotic with blood serum. Each 1 g of KCl represents 13.4 m moles of K. It should not contain less than 99% of KCl when determined by titration with standard $AgNO_3$ (Mohr's method).

KCl is used as an electrolyte replenisher, along with NaCl and calcium chloride. It may be administered orally as solution as well as in the form of elixir, mixture, intravenous infusion, injections, effervescent tablets, sustained release or extended release tablets, capsules. It is also

used in digitalis poisoning. Although K is a normal constituent of intracellular body fluids its administration may lead to complications hence precautions are needed.

Limits are prescribed for acidity, alkalinity, bromides, iodides, and heavy metals, Ca, Mg, As, Ba, Fe, sulphates and loss on drying at 105 ° C. A limit on the presence of sodium salts is placed by testing with potassium antimonite solution, which forms a precipitate, if sodium salts are present as impurity. Both preparations containing only KCl or KCl in conjunction with NaCl and dextrose are used in the treatment of hypokalemia.

$$NaCl + KSbO_3 \longrightarrow NaSbO_3 \downarrow + KCl$$

It is stored in well closed containers to prevent absorption of moisture.

Standard 0.1 N KCl solution: Prepare by weighing accurately about 7.5 g of KCl and dissolve in a 1 dm^3 graduated flask in water. For other details see preparation of 0.1 N standard NaCl solution.

Oral Rehydration Salts (ORS): This is recommended for infants and children who have been affected by excessive diarrhea or vomiting or any other type of dehydration. It contains, NaCl, KCl, $NaHCO_3$ and dextrose in a homogeneous powder. It is dissolved in a litre of pure drinking water and then given.

Potassium Bromide, IP: This is not official in the current IP (1996). This is the most important bromide and has a molecular weight of 119.0.

It is prepared in laboratory by the action of bromine on a hot and concentrated solution of caustic potash.

$$6KOH + 3Br_2 \longrightarrow 5KBr + KBrO_3 + 3H_2O$$

Pot. Bromate

The solution containing $KBrO_3$ is evaporated to dryness and the dried mass is ignited with charcoal to reduce it to bromide.

$$KBrO_3 + 3C \longrightarrow KBr + 3CO \uparrow$$

The ignited mass is extracted with warm water and the resulting liquid is filtered to remove charcoal and KBr is crystallized by the evaporation of the filtrate.

On a large scale first of all ferroso-ferric bromide Fe_3Br_8 ($FeBr_2.2FeBr_3$) is prepared by the action of iron and bromine. This is separated by filtration and boiled with a concentrated solution of K_2CO_3 when a mixture of black ferrous and ferric hydroxides is precipitated with the evolution of CO_2. KBr remains in solution which is concentrated and cooled to get the crystals:

$$3Fe + 4Br_2 \longrightarrow Fe_3Br_8$$

$$Fe_3Br_8 + 4K_2CO_3 \longrightarrow Fe(OH)_2.2Fe(OH)_3 \downarrow + 8KBr + 4CO_2 \uparrow$$

It is a colourless, odourless crystalline solid (or a white crystalline powder) with a slight saline bitter taste. It is freely soluble in water and glycerol but slightly soluble in alcohol. It can be determined by Volhard's method but chlorides and iodides interfere. The current edition of IP has introduced an oxidation method by $KMnO_4$ in acid medium at boiling temperature. Br_2 is set free and is expelled during boiling enabling the pink colour of permanganate to indicate the equivalence point.

$$10KBr + 2KMnO_4 + 8H_2SO_4 \longrightarrow 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5Br_2 \uparrow$$

Small amounts of chloride (less than 20 mg %) do not interfere, however, iodides and ammonium salts interefere.

KBr is used as a sedative and anti-convulsants. It is a toxic substance, and slow accumulation of Br^- ions in the body causes excessive depression of the central nervous system, skin rashes etc. These symptoms are also referred to as bromism. At present better and safer drugs have replaced KBr. NaBr in place of KBr is used if K^+ ion is contra-indicated in some patients.

Limits are prescribed for acidity, clarity of a 10% solution, bromates, iodides, heavy metals, As, Ba, Fe, sulphate, chlorides, Na, Ca, Mg and moisture.

Standard 0.1N KBr solution: Dissolve accurately weighed about 12.0g of dry and AR grade KBr in 1 dm^3 graduated flask in water. Also see the preparation of 0.1 N standard NaCl solutions.

Other standard solutions: i) Ammonium thiocyanate solution: The equivalent weight is the same as the molecular weight i.e. 76.0g. Hence for the preparation of an approximate 0.1 N solution of NH_4SCN, dissolve about 7.6 g of it, weighed upto two decimal places only in 1 dm^3 of water. These solutions are used as an intermediate and hence dissolve in water in a 1 dm^3 graduated cylinder. Now standardize it against 0.1N $AgNO_3$ solution using Volhard's method.

ii) KSCN solution: Prepare 0.1N solution of potassium thiocyanate by weighing about 9.8g of KSCN and dissolving the salt in water and then diluting the solution to 1dm^3. Use Volhard's method to standardize it.

Preparation of indicator solutions: i) Potassium chromate solution: Dissolve 19.4 g of K_2CrO_4 (AR grade) in a 1 dm^3 of water.

ii) Ferric alum indicator: This is a saturated solution of $Fe_2(SO_4)_3.Al_2(SO_4)_3.24H_2O$, ferric alum in the 1M HNO_3 acid. Dissolve 40 g of the solid in 100 cm^3 of distilled water having 6 cm^3 of conc HNO_3.

iii) Fluorescein indicator: Dissolve 0.1 g of fluorescein in 100 cm^3 of 70% alcohol.

iv) Dichlorofluorescein indicator: Dissolve 0.1 g dichlorofluorescein in 100 cm^3 of 70% alcohol. Fluorescein or its sodium salt can also be used in its place, and is similarly prepared.

Standardisation of Silver Nitrate and Potassium Thiocyanate Solutions:

Sodium or potassium chloride can be used as a primary standard for $AgNO_3$ solution. Either of the methods**, (Mohr's method- K_2CrO_4 indicator)** or dichlorofluorescein **(Fajan's method-adsorption indicator)** can be followed. When the $AgNO_3$ solution has been standardized with any one of these methods, this solution can be used to standardize potassium thiocyanate solution by **Volhard's method**. The two solutions are titrated directly, using Fe(III) as the indicator.

Procedure:

a) Mohr's method: Weigh accurately about 1.2 g of NaCl and dissolve the salt in water in a 250 cm^3 graduated flask. Pipette out an aliquot of 50 cm^3 into a clean 250 cm^3 conical flask.

Add 2 cm^3 of potassium chromate indicator (0.1 M). Place the $AgNO_3$ solution in burette and note down the initial reading. Now titrate the chloride solution with $AgNO_3$, swirling the titration mixture constantly, until the reddish colour of the silver chromate (Ag_2CrO_4) begins to spread more widely through the solution, indicating that the end point is almost reached. Furthermore the formation of bigger lumps of AgCl is also an indication that the end point is near. At this stage continue addition of $AgNO_3$ solution drop by drop until there is permanent colour change from the yellow of CrO_4^{2-} ions to the reddish colour of silver chromate precipitate. Run an indicator blank, if desired. Repeat the procedure in the form of two similar titrations so as to get atleast a concordant set of readings. **Calculate as:**

Let the weight of NaCl taken in 250 cm^3 0.1 N standard solution be = Wg

Normality of standard NaCl solution = 4W/ 58.5

Normality of $AgNO_3$ solution, N_{AgNO3}= 4W/ 58.5 * 50* $1/V_1$

Where, V_1 = volume of $AgNO_3$ solution used.

b) Fajan's method: Prepare NaCl or KCl 0.1N standard solution as discussed. Rinse and fill the burette with silver nitrate solution as usual. Pipette out 50 cm^3 of standard NaCl solution into a 250 cm^3 conical flask and add 10 drops of dichlorofluorescein indicator and 0.1 g of dextrin. The function of dextrin is to prevent coagulation of colloidal silver chloride. Now titrate with silver nitrate to the point where the colour of the dispersed AgCl changes from yellowish-white to a definite pink. The end point is easier to detect in diffuse light. The colour change is reversible and back titration is possible with a standard NaCl solution. Repeat the titration two times more

to get a concordant set of readings. Calculate the normality (N_{AgNO3}) of $AgNO_3$ solution as before.

c) Volhard's method: The titration will be carried out in HNO_3 medium. For use of HNO_3 in this titration it should be free from oxides of nitrogen so that it has no yellowish tinge, and is then called purified nitric acid. Dilute 150 cm^3 conc HNO_3 to 500 cm^3 with water and carefully boil to remove all lower oxides of nitrogen i.e., till it becomes colourless. Make up to 1 dm^3 with water in a graduated cylinder. A 10 cm^3 volume of this purified HNO_3 is used in each titration.

Pipette out 25 cm^3 of standard silver nitrate solution into 250 cm^3 conical flask, add 10 cm^3 of purified HNO_3 acid and 1 cm^3 of iron (III) alum indicator solution. Titrate with thiocyanate solution with constant swirling of the solution, until the reddish brown colour begins to spread throughout the solution. At this stage add thiocyanate solution drop by drop and shaking the solution after each addition. The end point is marked by the just permanent appearance of the reddish colour of the iron-thiocyanate complex.

$$Ag^+ + SCN^- \longrightarrow AgSCN \downarrow \text{(white ppt)}$$

$$Fe^{3+} + SCN^- \longrightarrow FeSCN^{2+} \text{(reddish-brown)}$$

Titrate two additional portions of $AgNO_3$ solution with thiocyanate to fix the titre value. Calculate the normality of KSCN solution:

Normality of KSCN* Volume of KSCN = Normality of $AgNO_3$* Volume of $AgNO_3$

$$N_{KSCN} * V_1 = 25* 4W/ 169.9$$

Where, V_1 = volume of KSCN used

And W= weight of $AgNO_3$ dissolved in preparing 250 $cm^3$of solution

$$N_{KSCN} = 25/V_1* 4W/ 169.9$$

Determination of Chloride

A direct titration of a chloride with $AgNO_3$ solution using either chromate ion (Mohr's method) or dichlorofluorescein (Adsorption indicator-Fajan's method) can be employed. alternatively, excess standard $AgNO_3$ solution can be added to the unknown and the excess back titrated with standard KSCN solution. It has been assumed that the sample of chloride is water soluble.

1. Determination of the strength of the given NaCI solution [approx. 0.1 N] by Mohr's method; prepare a standard 0.1 N $AgNO_3$ solution.

Reaction:

$$Ag^+ + Cl^- \longrightarrow AgCl^-$$

Appearance of a permanent reddish tinge (with K_2CrO_4 indicator) at the end point. The reaction with K_2CrO_4 is as:

$$Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4$$

Reddish tinge

The precipitate of $AgCrO_4$ is produced only after the complete precipitation of Cl^- as AgCl. $AgNO_3$ solution is contained in a burette.

Procedure: i) Preparation of standard 0.1 N solutions: Prepare a standard solution (N/10) of NaCl as already directed in this section.

ii) Preparation of 0.1 N $AgNO_3$ solutions: This solution may be provided by the instructor. If not, prepare a 0.1 N $AgNO_3$ solution as already directed in this section.

iii) Prepare 0.1 N K_2CrO_4 (indicator) solution as already instructed in this section.

Standardisation of $AgNO_3$ solution: Pipette out 25 cm^3 of standard 0.1 N NaCl solution (self prepared) into a 250 cm^3 conical flask and add 2 cm^3 of (0.1M) K_2CrO_4 indicator. Titrate it with $AgNO_3$ solution as directed before in this section. Note down the burette reading. Repeat the titration with two more aliquots of NaCl solution to fix the titre value. Let a volume, V_1 cm^3 of $AgNO_3$ is used here.

Standardisation of the unknown NaCl solution: Pipette out 25 cm^3 of the given (unknown) NaCl solution and titrate it against $AgNO_3$ solution by using 2 cm^3 of 0.1 M K_2CrO_4 as indicator till a reddish tinge is obtained. Repeat the titration to get 2-3 concordant readings. Let the volume of $AgNO_3$ solution used this time be V_2 cm^3.

Calculate as:

Let the weight of NaCl dissolved in 250 cm^3 (of 0.1 N standard solution) = W g

Normality of standard NaCl solution (N_{NaCl}) = 4W/ 58.5

Normality of $AgNO_3$ (N_{AgNO3}) = 4W/58.5 *25/V_1

Normality of unknown NaCl solution (N_{NaCl}) = 4W/58.5*25/V_1*V_2/25

Or, strength of NaCl = Equivalent weight* Normality

(in g/dm^3)

$$= 4W/58.5^* V_2/V_1{*}58.5 = 4W{*}V_2/V_1 g\ dm^{-3}$$

2. Determination by Fajan's method; use of adsorption indicator

Procedure: The preparation of solutions of NaCl, $AgNO_3$ etc. remains the same as before. For the preparation of indicator solution (dichlorofluorescein)

i) Standardisation of $AgNO_3$ solution: Pipette out 25 cm^3 of standard 0.1 N NaCl solution (self prepared) into a 250 cm^3 conical flask and add 10 drops of dichlorofluorescein indicator and 0.1 g of dextrin. Titrate with 0.1 N standard $AgNO_3$ solution as usual. Repeat the titration with 2-3 more aliquots of NaCl solution to get atleast two consecutive readings concordant. Let a volume V_1 cm^3 of $AgNO_3$ is used here.

ii) Standardisation of the unknown NaCl solution: Pipette out 25 cm^3 of the given (unknown) NaCl solution in a 250 cm^3 conical flask and add 10 drops of dichlorofluorescein indicator and 0.1 g of dextrin and titrate as usual with $AgNO_3$ solution and obtain at least a set of concordant readings. Let the volume of $AgNO_3$ solution used this time be V_2 cm^3. Calculate the strength of NaCl in g per dm^3 as before. Also calculate the percentage of chloride in the sample. In place of dichlorofluorescein the fluorescein or its sodium salt may also be used.

iii) Determination by Volhard's method: when KSCN or NH_4SCN solution is added to $AgNO_3$ solution in the presence of nitric acid and iron (III) alum as indicator, a white precipitate of AgSCN is first formed.

$$Ag+ + SCN- \longrightarrow AgSCN$$

When all the Ag^+ ions present in the solution have reacted completely i.e., the end point has reached, the addition of a drop of thiocyanate solution in excess produces a reddish-brown coloration of $FeSCN^{2+}$ complex.

$$Fe^{3+} + SCN^- \longrightarrow [FeSCN]^{2+`}$$

The precipitate of AgSCN formed in the solution has a tendency to adsorb Ag^+ ions, hence to avoid premature end point, the solution during the course of titration is throughout stirred. The titration is carried out in acid medium in order to prevent the hydrolysis of ferric iron. Further ferric alum rather than ferric sulphate has been chosen as indicator because of the stability of the double salt towards hydrolysis.

Procedure: The solutions of standard 0.1N $AgNO_3$ and 0.1N approximate KSCN or NH_4SCN will be prepared as usual. For the preparation of iron (III) alum indicator and for the preparation of purified nitric acid.

Pipette out 25cm^3 of the 0.1N approximate KSCN or NH_4SCN solution into a 250cm^3 conical flask, add 10cm^3 of purified nitric acid. Now go on adding $AgNO_3$ solution (from a burette) until an excess of about 5cm^3 is present. Add 1-2 cm^3 of nitrobenzene, stopper the flask with a rubber stopper and shake the flask vigorously for about 30-40 seconds until the AgCI is well coagulated. At this stage add 1cm^3 of iron (III) alum indicator solution and titrate the excess of $AgNO_3$ with

standard KSCN/NH_4SCN solution (in a burette). The end point is marked by the permanent appearance of the reddish-brown tinge of the iron thiocyanate complex. Titrate atleast two other aliquots in a similar manner to fix the titre value. Calculate the percentage of chloride in the sample.

Determinations by Volhard's Method Continued

1 (a) HCl content of commercial conc hydrochloric acid: The given solution of a chloride is treated with an excess of standard $AgNO_3$ solution and the residual $AgNO_3$ determined by titration with standardized thiocyanate solution. Now AgCl is more soluble than AgSCN and would liberate chloride ion:

$$AgCl_{(s)} + SCN^- \longleftrightarrow AgSCN_{(s)} + Cl^- \text{ (s = solid)}$$

Hence, it is necessary to remove silver chloride by filtration. HCl acid is usually 11-12 N and must be diluted before this determination. Measure out accurately either by means of a rubber bulb fitted suction pipette 10 cm^3 of conc HCl into a 1 dm^3 graduated flask and make up to the mark with chloride free distilled water. Shake well to make it homogeneous. Pipette out 25 cm^3 of this HCl solution into a 250 cm^3 conical flask, add 5 cm^3 of 6M-HNO_3 and then 30 cm^3 of standard 0.1 N $AgNO_3$ solution. AgCl is precipitated; it is better to boil it for a few minutes to coagulate AgCl and thus remove most of the adsorbed Ag^+ ions from its surface before filtration. Filter through a sintered glass crucible and wash thoroughly with very dilute HNO_3. Collect whole of the filtrate and washings together quantitatively into a 350 cm^3 conical flask. Add 1 cm^3 of the ferric alum indicator and titrate the residual $AgNO_3$ with standardized 0.1 N thiocyanate solution. Find out the volume of $AgNO_3$ solution that has reacted with the hydrochloric acid and then the percentage of HCl in the sample used.

b) Bromides: These can be determined by Volhard's method. Here AgBr is less soluble than AgSCN, hence it is not necessary to filter off its precipitate. The given bromide solution is acidified with dilute HNO_3, as above, the excess of standard 0.1N $AgNO_3$ determined with standardized 0.1M-KSCN or NH_4SCN using ferric alum solution as indicator.

c) Iodides: These can be determined by Volhard's method. Here too there is no need to filter off the precipitate of AgI since it is very much less soluble than AgSCN. However, the iodide solution must be very dilute so that the adsorption effects are negligible. The dilute iodide solution (about 2.25 of an iodide salt per 250 cm^3 of the solution), acidified with dilute HNO_3, is treated dropwise shaking vigorously with standard 0.1N-$AgNO_3$ until the yellow precipitate coagulates and settles so that the supernatant liquid becomes clear and colourless. $AgNO_3$

solution is then present in excess. At this stage add 1 cm^3 of ferric alum indicator and titrate the remaining silver nitrate with standard 0.1 M-KSCN or NH_4SCN as usual.

2. Determination of the percentage purity of a sample of KCl: 8g of which has been dissolved per dm^3; provided 0.1 N $AgNO_3$ solutions.

Procedure: Pipette out 25 cm^3 of the KCl solution in a 250 cm^3 conical flask, add 10 drops of sodium dichlorofluorescein indicator and 0.1 g of dextrin. Titrate with 0.1 N standard $AgNO_3$ solution from a burette, in small lots and with constant vigorous shaking in the diffused light until the precipitate of silver chloride shows a change in colour from yellowish-green to pinkish red. This is the end point. Repeat the titration to get atleast a concordant set of readings. Calculate as:

% purity of KCl (in sample) = V*0.1 N*1/25*75.55*100/8%

Where, V = volume of $AgNO_3$ solution used,

And 0.1 N = Normality of the $AgNO_3$ solution.

3. Determination of the percentage composition of a mixture of KCl and NaCl using 0.1 N standards $AgNO_3$: Mohr's method is being used here for this determination. The reactions are:

$$2AgNO_3 + KCl + NaCl \longrightarrow 2AgCl + KNO_3 + NaNO_3$$

Ionically: $Cl^- + Ag^+ \longrightarrow AgCl$

Indicator is K_2CrO_4 and a reddish tinge will appear at the end point due to the formation of red colour of Ag_2CrO_4 precipitate.

Procedure: i) Prepare a standard solution of mixture by dissolving an accurately weighed amount of it in a 250 cm^3 graduated flask. Let it be W g.

ii) Titrate it against the given $AgNO_3$ solution by taking 25 cm^3 of the solution in a 250 cm^3 conical flask and adding K_2CrO_4 indicator as usual until a reddish-brown tinge is obtained.

Calculate as:

Let V be the volume of N/10 $AgNO_3$ solution required for 25 cm^3 of the chloride mixture.

$$N_{Mixture} = N_{AgNO3} * V_{AgNO3} / V_{Mixture} = 1/10 * V/25 = V/250$$

Let the amount of NaCl present in 250 cm^3 of the mixture be X g, then, the strength of NaCl = 4*X g per dm^3

$$N_{NaCl} = 4X/58.5$$

Similarly, $N_{KCl} = 4(W-X)/74.5$

Also, $N_{Mixture} = N_{NaCl} + N_{KCl}$

$$V/250 = 4X/58.5 + 4(W-X)/74.5$$

Knowing W and V, X can be calculated. Then,

% of NaCl = X/W*100; % OF KCl = W-X/W*100

4. Determination of the percentage purity of a given sample of KI; provided 0.1 N $AgNO_3$ and 0.1 N KCNS solutions: A known quantity of KI is dissolved in 250 cm^3 of water. A known volume of this is now treated with a known excess of $AgNO_3$ solution. Silver iodide would precipitate out as a pale yellow solid. The excess of residual $AgNO_3$ is then back titrated with KSCN solution using ferric alum as indicator. The reactions taking place are:

$$KI + AgNO_3 \longrightarrow \underset{\text{Yellow}}{AgI\downarrow} + KNO_3$$

$$AgNO_3 + KSCN \longrightarrow \underset{\text{White}}{AgSCN\downarrow} + KNO_3$$

Procedure: Dissolve about 4.0 g of KI into a 250 cm^3 graduated flask in water and make it upto the mark. Shake well to make it homogeneous. Pipette out 25 cm^3 of KI solution into a 250 cm^3 conical flask and add about 35 cm^3 of 0.1 N $AgNO_3$ solution, followed by the addition of 2 cm^3 of 5 N HNO_3 acid. Slightly warm the solution to coagulate the precipitate of AgI formed. In this condition it settles to the bottom and does not float on the surface. Cool the solution and at this stage add 1 cm^3 of ferric alum indicator. Rinse and fill the burette with KSCN solution. Start titration to the point when a permanent faint reddish –brown tinge is just obtained. Repeat the titration to get three concordant readings. Calculate as:

Strength of KI solution = 4*W g/dm^3

Where, W = wt of KI dissolved in 250 cm^3

Let V_1 cm^3 of KSCN solution is required to react the residual $AgNO_3$ solution. Thus V_1 cm^3 will also be equal to the amount of residual $AgNO_3$ solution. Hence the volume of $AgNO_3$ solution which has actually reacted with KI solution = (35-V_1) cm^3

Normality of KI, N_{KI} = 35-V_1/10*10 = 35-V_1/100

Strength of KI = 35-V_1/100*166 g/dm^3

% purity of KI sample = 35-V_1/100*166*100/4W

= 35-V_1/4W*166

5. Determination of the amount of HCl and HNO_3 acids present together in a given solution: The mixture is titrated against standard alkali using phenolphthalein as indicator. This gives the total normality of both the acids. In the second titration, the acid mixture is first neutralized by calcium carbonate and then titrated with standard $AgNO_3$ solution using K_2CrO_4

as indicator. This gives the normality of HCl only. The normality of HNO_3 acid can then be obtained by difference. Thus the composition of the mixture can be known. The reactions taking place are:

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2 \uparrow$$

$$CaCO_3 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2 \uparrow$$

$$2AgNO_3 + CaCl_2 \longrightarrow Ca(NO_3)_2 + 2AgCl \downarrow$$

Procedure: i) Rinse and fill the burette with the given acid mixture. Pipette out 25 cm^3 of 0.1 N NaOH solutions into a 250 cm^3 conical flask. Add 2-3 drops of phenolphthalein indicator. The mixture will develop a red-pink colour. Titrate it with the acid till it becomes just colourless. Repeat the titrations 2-3 times to get concordant readings.

ii) Rinse and fill the burette with 0.1 N $AgNO_3$ solution. Pipette out 25 cm^3 of the acid mixture into a clean 250 cm^3 conical flask. Add pinch by pinch solid AR calcium carbonate till evolution of CO_2 gas ceases and then add a little more of $CaCO_3$. Now add 1 cm^3 of K_2CrO_4 solution indicator and titrate with $AgNO_3$ solution till a permanent light reddish-brown precipitate or colour is just obtained. Repeat the process and get 2-3 concordant readings. Calculate as:

Let 25 cm^3 of 0.1 N NaOH = V_1 cm^3 of the acid mixture

$$N_{Mixture} = 25*0.1*1/V_1 = 2.5/V_1$$

Let 25 cm^3 of the neutralized mixture requires V_2 cm^3 of 0.1 N $AgNO_3$ solution. Then,

$$25*N_{HCl} = V_2*0.1$$

$$N_{HCl} = V_2/250$$

Now the normality of HNO_3 alone is given by:

$$N_{HNO3} = N_{Mixture} - N_{HCl}$$

$$= 2.5/V_1 - V_2/250$$

The strength of HCl = $V_2/250*36.5$ g per dm^3

And, the strength of HNO_3 = $[2.5/V_1 - V_2/250]$ 63.0129 g/dm^3

Determination of end points in precipitation reaction

Many methods are utilized in determining end points in these reactions, but only the most important will be mentioned here.

Formation of a coloured precipitate (Mohr method):

An example of the use of formation of second highly coloured precipitate for detection of end point is the Mohr's method for determination of chloride and bromide ions with silver nitrate.

Here, chromate ion is the indicator; the end point is detected by the appearance of brick red silver chromate (Ag_2CrO_4) in neutral medium, The molar solubility of silver chromate is several times greater than that of silver chloride or bromide.

Thus silver chloride tends to form first in the titration mixture. By adjusting the chromate concentration to a suitable level, formation of silver chromate can be retarded until the silver ion concentration in the mixture is equal to the theoretical equivalence point for chloride. This can be easily determined as follows

At equivalence point: $[Ag+] = [Cl-] = \sqrt{AgCl}$

$$[Ag+] = 1.05 \times 10^{-5}$$

The chromate concentration required to initiate precipitation of silver chromate under these condition can be also calculated from its solubility product:

$KSp_{Ag2CrO4} = [Ag+]^2 [CrO_4^{2-}]$

$[CrO_4^{2-}] = KSp/ [Ag^+]^2 = [1.1x10^{-12}]/ [1.5 \times 10^{-5}]^2 = 10^{-2}$

This means that the concentration of chromate necessary to give the brick red of silver chromate at equivalence point is 0.01 M in fact it is 0.015M exactly.

Interferences and limitations of Mohr method:

1. The Mohr titration is applicable only in neutral or faintly alkaline solution with pH values from about 6 to 10. In acid solution, the CrO_4^{2-} concentration is greatly decreased according to the following equilibrium:

$$2H+ + 2\ CrO_4^{2-} \rightarrow 2\ HCrO_{4-} \rightarrow\ Cr_2O_7^{2-} + H_2O$$

and dichromate is formed whose silver salt is soluble. Therefore, no indicator precipitate forms. If, on the other hand, the medium is alkaline, silver will precipitate as its oxide:

$$2\ Ag+ + 2\ OH^- \rightarrow 2\ AgOH \rightarrow\ Ag_2O + H_2O$$

This interferes with the titration, the silver oxide may even precipitate before silver chromate especially where the solubility product of Ag_2O is exceeded. If ammonium salts are present, the pH of the solution must not exceed pH 8 otherwise free ammonia will be produced and dissolve

the silver chloride precipitate. Therefore, the halide solution should be neutralized before titration if necessary, by adding $NaHCO_3$ or dilute HNO_3, as the case may be.

2. Cations which give insoluble chromate e.g. barium ions: They must be absent or removed before the titration.

3. The reverse titration of silver ion with chloride ion using chromate as indicator is not feasible, the flocculated Ag_2CrO_4 formed initially, reacts slowly with chloride especially near the end point of the titration. However to determined silver by Mohr method, it is possible to add excess standard chloride solution and then back-titrate using the chromate indicator.

4. Titration of iodide; and of thiocyanate is not successful because silver iodide and silver thiocyanate adsorb chromate ions so strongly that a false and somewhat indistinct end point is obtained.

Formation of a soluble coloured compound (Volhard method):

This procedure is exemplified by the method of Volhard for the titration of silver in the presence of free nitric acid with standard potassium or ammonium thiocyanate solution. The indicator is a solution of ferric nitrate or of ferric ammonium alum. The addition of the thiocyanate solution produces first a precipitates of silver thiocyanate (S.P. 7.I x $l0^{-13}$).

$$Ag+ + SCN- \rightarrow AgSCN$$

When this reaction is complete, the slightest excess of thiocyanate produces a reddish-brown colouration, due to the formation of the complex ferrithiocyanate ion:

$$Fe+++ + SCN- \rightarrow [FeSCN]++$$

This method may be applied to the determination of chlorides, bromides, and iodides in acid solution. Excess of standard silver nitrate solution is added, and the excess is back-titrated with standard thiocyanate solution. For the chloride estimation, we have the following two equilibria during the titration of excess of silver ions:

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

$$Ag+ + SCN^- \rightarrow AgSCN$$

COMPLEXOMETRIC TITRATION

INTRODUCTION

- Complexometric titration (sometimes chelatometry) is a form of volumetric analysis in which the titration based on complex formation between the analyte and titrant and these colored complexes is used to indicate the end point of a titration.
- Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution. An indicator with a marked color change is usually used to detect the end-point of the titration.
- A complexometric titration is one in which a soluble, undissociated, stoichiometric complex is formed during the addition of a ligand solution (titrant) to the solution of metal ion under suitable pH conditions.
- The quick formation and stability of complex have been found the most important criterion for the complexometric titration.
- Since a single stoichiometric complex is not formed in one step therefore a single stoichiometric point is not observed.
- The polyamino carboxylic acids have been found to be useful as titrants.

These chelating agents satisfy the type of properties required as successful titrant ie

a) Formation of a stable and soluble complex
b) A stoichiometric complex with the metal ions in single step
c) Should be selective in nature.

THEORY

Any complexation reaction in theory be applied as a volumetric technique provided that:

1. The reaction reaches equilibrium rapidly after each portion of titrant is added.

2. Interfering situations do not arise (such as stepwise formation of several different complexes of the metal ion with the titrant, resulting in the presence of more than one complex in solution during the titration process).

3. A complexometric indicator capable of locating equivalence point with fair accuracy is available.

COMPLEX

It is a compound that is formed by the combination of a metal ion with a molecule that is capable of donating electrons for example:

$[Cu(NH_3)_4]^{2-}$ $[Co(NH_3)_6]^{3+}$

Cupric ammonium ion Cobaltamine

In the above two examples both Cu^{2+} and Co^{2+} form complexes with lone pair of electrons present in the neutral molecule ammonia eg NH_3.

CHELATE

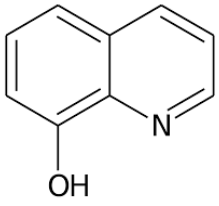
It is a complex formed between the ligand containing two or more donor groups and metal to form ring structure. When a chelate takes place and 5 or 6 membered ring was formed through oxygen or nitrogen atoms. These rings are generally more stable.

Chelating agents: organic molecules containing two or more donor groups which combine with metal to form complex are having ring structure.

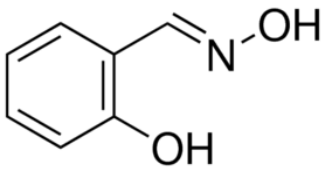
Sequestering agent: Ligands which form water soluble chelates (e.g. EDTA), they are used to liberate or solubilize metal ions. The agents which form water insoluble chelates are used to remove the metal ions from solution by precipitation.

Example

1. Disodium ethylenediaminetetraacetate (EDTA) reacts with polyvalent metal ions to result in the formation of a fairly stable water-soluble complex or a chelate compound.
2. 8-Hydroxy quinoline, salicylaldomine are chelating agents forming water insoluble complex.



8-Hydroxy quinoline

B 

salicyaldomine

LIGAND

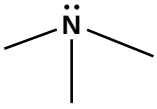
Complexing agent is any electron donating ion or molecule usually called ligands which have ability to form one or more covalent or dative bond with the metal ion.

Ligands or complexing agent can be any electron donating group which has the ability to bind with metal ion producing a complex ion.

Ligands are Lewis bases and can bind proton as well as metallic cation. Ligands may be classified on the basis of number of points of attachment to the metal ion.

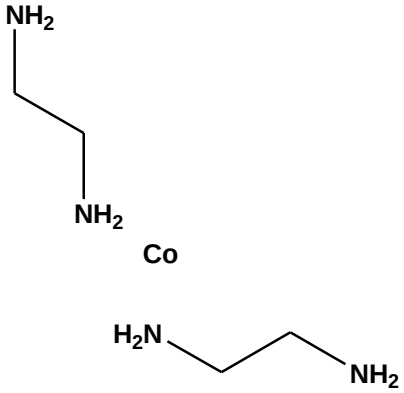
1. Monodentate Ligands:- The ligand is bound to the metal ion at only one point by the donation of a lone pair of electron to the metal.

Eg: NH3 is a example for monodentate ligand, which form complex with cupric ion according to the equation



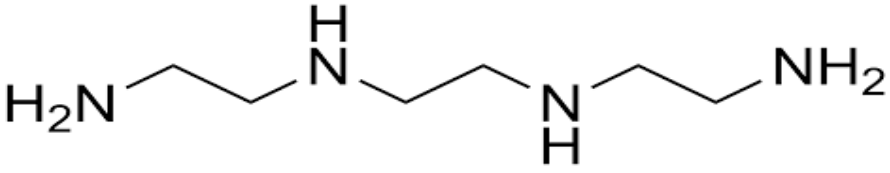
2. Bidentate Ligand:- The ligand molecule or ion has a lone pair of electron, then the molecule has two donor atom and it may be possible to form two coordinate bonds with the metal ion is known as bidentate ligand.

Example: bis(ethylenediamine) cobalt (III) complex



3. Multidentate Ligands:- Ligand contains more than two coordinate atoms per molecule.

Example: Triethyl tetramine is quadrientate ligand which for complex with copper by attachment with four nitrogen atom.



4. Another important type of complex, a macrocycle is formed between a metal ion and a cyclic organic compound. The selectivity of a ligand for one metal ion over another relates to the stability of the complexes formed. The higher the formation constant of a metal-ligand complex,

the better the selectivity of the ligand for the metal relative to similar complexes formed with other metals.

Stability of complex

Generally the formation of a 1:1 chelate complex (MX) may be designated by the following equation

Where M= Metal ion and X= Chelating ion

Hence, the stability constant K, may be expressed as

K=[MX]/[M][X]

There are two cardinal factors which influence the stability constant (K) namely

a) Elevation in temperature affords a slight enhancement in the ionization of the complex and a slight lowering of K
b) Stability constant is decreased on the addition of electrolytes with no common ion, whereas ethyl alcohol enhances K, perhaps on account of the suppression of ionization.
c) In Complexometric titration the formation of stable, soluble complex is the driving force in the reaction. The stability of complex influenced by
    1. Activity of metal ion. For example monovalent ion like sodium gives relatively weak complex.
    2. pH at which titration is carried out.
    3. Organic solvent which influence the stability of the complex.

Factors influencing the stability of complexes:-

a) Complexing ability of metals
b) Characteristics of the ligand

1. The basic strength of ligand
2. It's chelating properties
    a. Steric effect
    1. Special requirement of ligand
    2. Distance between coordination sites
    3. Size of central ions

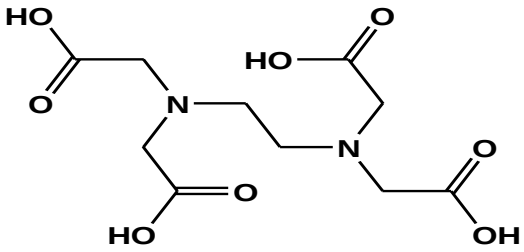
b. Nature of the ligand

c. Resonance effect

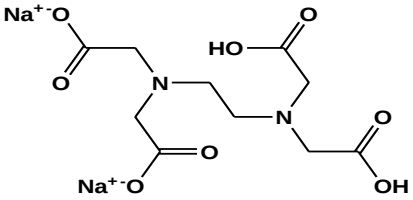
Complexing Agent/ Titrant

A large number of inorganic and organic titrants have been used in Complexometric titrations. These include

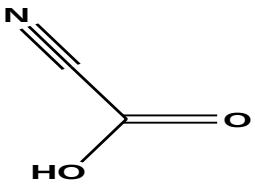
1. **Ethylenediaminetetraacetic acid**



2. **Disodium Ethylenediaminetetraacetic acid**



3. **Nitriloacetic acid (NITA)**



Among above said complexing agent EDTA has widely been used in the form of disodium salt as a titrant for the determination of almost all metalation and many anions directly or indirectly.

Disodium edetate is much more water soluble, non hygroscopic and very stable. Compounds containing the grouping -N(CH2COOH)2 are sometimes called complexones. Disodium edetate is called complexone II. The water should be metal free so the distilled water was used for the preparation of solution. Solution is best stored in polyethylene containers. It chelates with many di, tri and tetravalent cations to form complexes.

The reason for versatility of disodium EDTA

1. It forms soluble, stoichometric 1:1 complexes with metal ions.
2. The end point is readily detected by using suitable method.
3. On the basis of stability constant and control of pH of solution, the metal ion in EDTA titration can be divided into three groups

Group I: Metal ions in this group are titrated in basic condition. pH should maintain between 8-11. The metal ions are Magnesium, Calcium and Barium

Group II: Metal ion in this group is titrated against in acidic to slightly basic condition. pH is 4-7 the metal ions are Manganese, copper, iron, zinc.

Group III: Metal ion in this group is titrated against in acidic condition pH is 1-4 the metal ion include mercury, bismuth, cobalt and titanium

Method of end point detection

The most common way to follow Complexometric titration is either with a potentiometer and electrode designed to sense the metal involved or by using a metal ion indicator.

1. Metal Ion Indicators (pM indicator)

Metal ion indicators is a dye which forms a complex with metal that have one colour when it binds with metal ion but it may have different colors when it is not bound to the metal ion. All of the indicators have several acid base functionalities and the ionization state of these functional groups affects the colour of the unbound indicator. Thus the colour of the unbound indicator will vary with the pH of the solution.

The equivalence point in Complexometric titrations is invariably observed by the help of pM indicators. The relationship amongst pM indicator, concentrations of ligand, chelate complex and stability constant may be established by the following equations

Assuming K as the stability constant, we have

K= [MX]/[M][X]

Or [M] = [MX]/[M][K]

Or log[M] = log [MX]/[X]-log K

Or p[M] = log[X]/[MX]-pK ……(a)

Now, considering Eq.(a) if a solution is made in such a manner that [X] = [MX] we have

pM = -pK

Or pM= pK'. …… (b)

Where K'is the dissociation constant. This means that in a solution containing equal activities of metal complex and free chelating agent, the concentration of metal ions will remain roughly constant and will be buffered in the same way are hydrogen ion in a pH buffer. Various chelating agents are mostly basic in character therefore the equilibrium attained in a metal buffer solution is largely influenced by a change in pH. Hence, it may be concluded that the amino acid type chelating agents such as: ethylenediamine tetraacetic acid and ammoniatriacetic acid when [X]= [MX], pM increases proportionately with pH until it reaches a value pH 10 thereby attaining a constant value. Hence, this particular pH is the Ideal pH at which Complexometric titrations of metals with chelating agents in buffered solution must be performed.

Some important properties of these dyes to be useful as metal indicator are given as follows

It should be sufficiently stable. Otherwise colour change is not observed.

Metal indicator complex should be less stable than metal EDTA complex. This leads to the liberation of indicator giving sharp end point and rapid colour change.

The colour reaction should be such that before the end point of solution is strongly coloured.

The indicator should be sensitive to metal ion concentrations

The colour reaction should be specific.

Classification and example of pM indicator

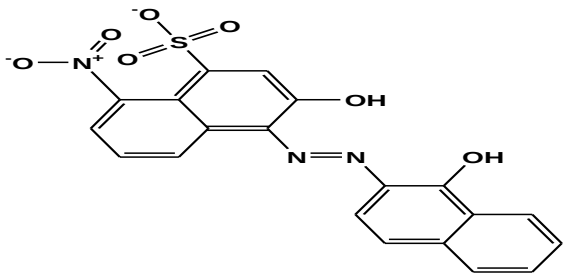
These metal ion indicator can be classified into according to the chromophore responsible for colour reaction. They are

1. Hydroxyl azo compounds, Mordant black T, Solochrome dark -blue (Calvin)
2. Phenolic compound and hydroxy substituted triphenyl methane compounds Xylenol orange, methyl thymol blue
3. Compound containing an amino methyl dicarboxy methyl group alizarin fluorine blue
4. Miscellaneous Diphenyl carbazone, Murexide

1. **Mordant Black T (Erichrome Black T, Solochrome Black T)**

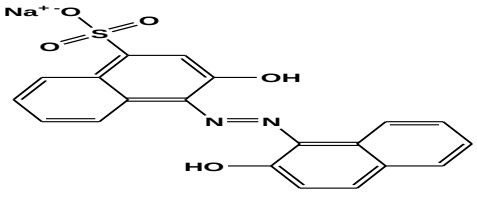
Chemically it is 1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sulphonate

0.2 g of dye with 2g of hydroxylamine HCl in 50 ml of methylamine HCl and 50 ml methyl alcohol is employed in titration .Useful in any titration were pH range is between 7 and 10, including calcium, magnesium and zincEBT is triprotic and has a different structure at varying pH valuesBetween pH 7 and 10 it exists as the dian ion and is blue in colour.It forms a red-purple complex with metals at pH 10 pH below 6.3 and above 11.5 it produce reddish colour It cannot be used in presence of either oxidizing or reducing agent and also ions like copper, aluminium, nickel, silver as these forms more stable complex with indicator than with complexing agent.



2. **Solochrome dark-blue (Calcon)**

Chemically it is sodium-2-hydroxy-1-(2-hydroxy-1-naphthylazo)naphthalene-4-sulphonate. It is brownish black powder with violet sheen. The indicator solution was prepared by dissolving 0.2gm of the dye in 50 ml of methanol. It gives purple red colour with calcium ion in alkaline solution. The free indicator is blue in colour in EDTA solution.It is used to assay calcium chloride, calcium carbonate and calcium gluconate



3. **Xylenol orange**

It is chemically 3,3’-bis-N,N-di(carboxymethyl)aminoethyl-o-cresol sulphonaphthalein

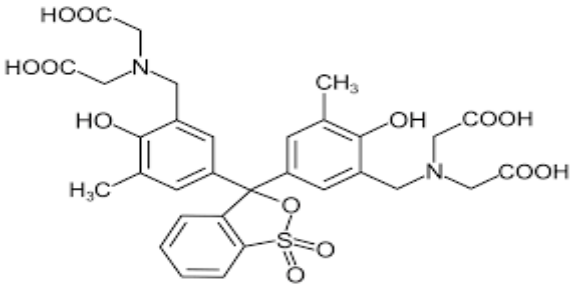
It retains the acid-base properties of creol red and displays metal indicator properties even in acid solution.It is yellow colour in acid solution and red colour in alkaline solution .The indicator solution is prepared by dissolving 0.1gm in 100 ml of water. Alternatively for storage one part of

Xylenol orange is dissolved in 99 part of potassium nitrate.It's pH range vary from 4-7.Solid hexamine used as buffering agent titration.

The metal complex is red in colour. Hence their use is restricted to titrating metals whose edetate complex is more stable in acid solution

It gives violet colour with mercury, lead and zinc in alkaline solution. Free indicator gives yellow colour in EDTA solution

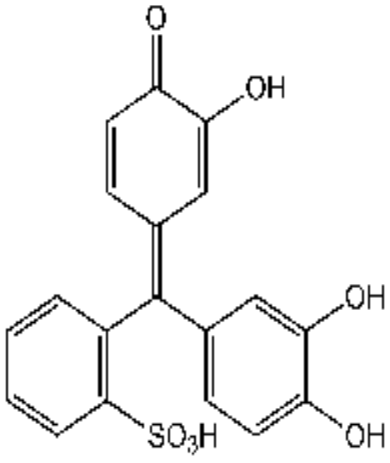
It is used in the estimation of aluminium hydroxide gel, aluminium sulphate



4. Catechol violet

It form highly coloured complex with wide range of metals 0.1% solution in water is employed as indicato .Catechol violet has advantage that it is very stable in aqueous solution. Complex with metals are blue in alkaline solution and also acidic solution

The pH range is 4-7. It is used to estimate Mg, Mn, Co, Zn, Ca and Cd ions.



2. pH indicator

Complex is stable in acidic media and reaction goes to completion even in presence of acid then the quantitatively produced acid can be titrated with standard alkali using acid base indicator. Methyl orange and methyl red is used as an indicator

3. Instrumental method for detecting end point

The following instrument methods are employed in the detection of end point during Complexometric titration, these are

Potentiometric titration

Photometric titration

Amperometric titration

Types of EDTA titrations

1. Direct titration

It is simple and most convenient method in EDTA titration. The solution containing the metallic salt is buffered to the desired pH and titrated directly with the standard EDTA solution with suitable pM indicator until the indicator colour change. It may be necessary to prevent precipitation of the hydroxide of the metal by the addition of some auxiliary complexing agent such as tartrate or citrate or triethanolamine

A blank titration may be performed for omitting the sample as a check on the presence of traces of metallic impurities in the reagents. The following metal ions such as Ca, Mg and Zn are directly estimated by direct titration method.

Examples

Magnesium trisilicate, magnesium hydroxide, zinc oxide and cream, magnesium sulphate, zinc stearate, zinc sulphate

Assay of Magnesium sulphate

CSynonyms- Epsom salts

Molecular formula- $MgSO_4.7H_2O$

Molecular weight- 246.5 gm

Magnesium sulphate contains not less than 99.0 percent and not more than 100.5% of $MgSO_4$ calculated on the dried basis.

Description

Colourless crystals or a white, crystalline powder

Preparation and standardization of 0.05 M disodium EDTA

Preparation: Dissolve 18.6 g of disodium edetate in sufficient water to produce 1000 ml. Standardize the solution in the following manner.

Standardization of 0.05 M Disodium EDTA

Weigh accurately about 0.8gm of granulated zinc and dissolve by gentle warming in 12 ml of dilute Hydrochloric acid and 0.1 ml of bromine water. Boil to remove excess bromine, cool and add sufficient water to produce 200 ml. Pipette 20 ml of the resulting solution into a flask and nearly neutralise with 2 M sodium hydroxide. Dilute to about 150 ml with water add sufficient ammonia buffer pH 10.0 to dissolve the precipitate and add 5 ml in excess. Add 50 mg of mordant black II mixture and titrate with the disodium edetate solution until the solution turns green. 1 ml of 0.1 M disodium edetate is equivalent to 0.000654 g of Zn.

Assay:- Weigh accurately about 0.3g, dissolve in 50 ml of water, add 10 ml of strong ammonia-ammonium chloride solution and titrate with 0.05 M disodium edetate, using b0.1g of mordant black II mixture as indicator, until a blue colour is obtained. 1 ml of 0.05 M disodium edetate is equivalent to 0.00602 g of MgSO4.

Back-titration or Residual titration

Many metals like aluminium forms hydroxide for various reasons cannot be titrated directly and they may precipitate from the solution in the pH range necessary for the titration or they may form inert complexes or a suitable metal indicator is not available. In such cases an excess of standard EDTA solution is added the resulting solution is back titrated with a standard metal ion solution such as zinc chloride or sulphate or of magnesium chloride or sulphate is often used for this purpose. The end point is detected with the aid of the metal indicator which responds to the zinc or magnesium ions introduced in the back titration.

Example

Aluminium glycinate, Dried aluminium hydroxide, aluminium sulphate, Bismuth sub carbonate

Assay Aluminium Hydroxide Gel

Synonyms:- Aluminium Hydroxide suspension or aluminium hydroxide mixture

Molecular formula Al2O3

Aluminium hydroxide gel is an aqueous suspension of hydrated aluminium oxide together with varying quantities of basic aluminium carbonate and bicarbonate. It may contain glycerin, sorbitol, sucrose or saccharin as sweetening agents and peppermint oil or other suitable flavours. It may also contain suitable antimicrobial agents.

Aluminium hydroxide gel contains not less than 3.5 percent and not more than 4.4 percent w/w of Al2O3.

Description: A white, viscous suspension, translucent in thin layers, small amounts of clear liquid may separate on standing.

Assay: Weigh accurately about 5.0g and dissolve in 3 ml of Hydrochloric acid by warming on a water-bath, cool to below 20degree celcius and dilute to 100.0 ml with water. To 20.0 ml of this solution, add 40.0 ml of 0.05 M disodium edetate, 80 ml of water, and 0.15 ml of methyl red solution and neutralise by the dropwise addition of 1 M sodium hydroxide. Warm on a water-bath for 30 minutes, add 3 g of hexamine and titrate with 0.05 M disodium edetate is equivalent to 0.002549g of Al2O3.

Replacement or substitution titration

Substitution titration may be used for metal ions that do not react with a metal indicator or for metal ions which form EDTA complexes that are more stable than those of other metals such as magnesium and calcium. According to the following equation replacement titration involves the quantitative displacement of second metal from a complex by the metal being determine. Then freed second metal is directly titrated with standard EDTA solution.

An interesting application is the titration of calcium. In the direct titration of calcium ions, Solochrome black gives a poor end point, if magnesium is present, it is displaced from its EDTA complex by calcium and an improved end point results.

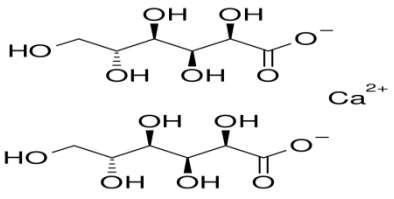
Example

Assay of Calcium Gluconate

Molecular formula: C12H22CaO14.H2O

Molecular weight: 448.40gm

Structure



Calcium gluconate is calcium D-gluconate monohydrate. Calcium Gluconate contains not less than 98.5 per cent and not more than 102% of C12H22CaO14.H2O

Description: A white, crystalline powder or granules

Assay

Weigh accurately about 0.5gm of sample and dissolve in 50 ml of warm water and cool, then add 5.0ml of 0.05M magnesium sulphate and 10 ml of strong ammonia solution and titrate with 0.05

M disodium edetate using mordant black II mixture as indicator. From the volume of 0.05 M disodium edetate required subtract the volume of the magnesium sulphate solution added. 1ml of 0.05 M disodium edetate is equivalent to 0.02242 g of C12H22CaO14.H2O.

Alkalimetric titration

When a solution of disodium ethylenediaminetetraacetate is added to a solution containing metallic ion and the complexes are formed with the liberation of two equivalents of hydrogen ion. The hydrogen ions thus set free can be titrated with a standard solution of sodium hydroxide using an acid-base indicator or a potentiometric end point. Alternatively an iodate-iodide mixture is added as well as the EDTA solution and the liberated iodine is titrated with a standard thiosulphate solution. The solution of the metal to be determined must be accurately neutralized before titration.

Masking Agents

EDTA is a very unselective reagent because it complexes with numerous doubly, triply and quadruply charged cations. When a solution containing two cations which complex with EDTA is titrated without the addition of a complex-forming indicator and if a titration error of 0.1 percent is permissible then the ratio of the stability constants of the EDTA complexes of the two metals M and N must be such that KM/KN> 106 if N is not to interfere with the titration of M. Strictly of course the constants KM and KN considered in the above expression should be the apparent stability constants of the complexes. If complex-forming indicators are used then for a similar titration error KM/KN> 108. The following procedures will help to increase the selectivity.

a) Suitable control of the pH of the solution: This of course makes use of the different stabilities of metal-EDTA complexes. Thus bismuth and thorium can be titrated in an acidic solution with Xylenol orange or methyl thymol blue as indicator and most divalent cations do not interfere. A mixture of bismuth and lead ions can be successfully titrated by first titrate with the bismuth at pH 2 with xylenol orange as indicator and then adding hexamine to raise the pH to about 5.

b) Use of masking agents: Masking may be defined as the process in which a substance without physical separation of it or it’s reaction products is so transformed that it does jnot enter into a particular reaction. Demasking is the process in which the masked substance regains its ability to enter into a particular reaction. By the use of masking agents some of the cations in a mixture can often be masked so that they can no longer react with EDTA or with the indicator.

An effective masking agent is the cyanide ion, this forms stable cyanide complexes with the cations of CD, Zn, Hg(II), Cu, Co, Ni, Ag and the platinum metals but not with the alkaline earths, manganese and lead.

c) Selective demasking: The cyanide complexes of zinc and cadmium may be de masked with formaldehyde-acetic acid solution or better with chloraal hydrate. The use of masking and selective demasking agents permits the successive titration of many metals. Thus a solution containing Mg, Zn and Cu can be titrated as follows:

1. Add excess of standard EDTA and back titrate with Standard Mg solution using Solochrome black as indicator. This gives the sum of all the metals present.
2. Treat an aliquot portion with excess of KCN and titrate as before. This gives Mg only.

d) Classical separation: These may be applied if they are not tedious thus the following precipitates may be used for separations in which after being redissolved the cations can be determined complexometrically nickel dimethylglyoximate, Mg(NH4)PO4.6H2O and CuSCN.

e) Solvent extraction: This is occasionally of value. Thus zinc can be separated from copper and lead by adding excess of ammonium thiocyanate solution and extracting the resulting zinc thiocyanate with 4-methylpentan-2-one, the extract is diluted with water and the zinc content determined with EDTA solution.

f) Choice of indicators: The indicator chosen should be one for which the formation of the metal-indicator complex is sufficiently rapid to permit establishment of the end point without undue waiting and should preferably be reversible.

g) Removal of anions: Anions such as orthophosphate which can interfere in Complexometric titrations may be removed using ion exchange resins.

h) Kinetic masking: This is a special case in which a metal ion does not effectively enter into the complexation reaction because of its kinetic inertness. Thus the slow reaction of chromium (III) with EDTA makes it possible to titrate other metal ions which react rapidly without interference from Cr(III) this is illustrated by the determination of iron(III) and chromium(III) in a mixture.

Demasking agents

It is the substance which releases the masked metal and the released substance Regins its ability to enter the particular reaction. This enables to determine a series of metal ion in one solution containing many cation.

Example: Formaldehyde and chloralhydrate

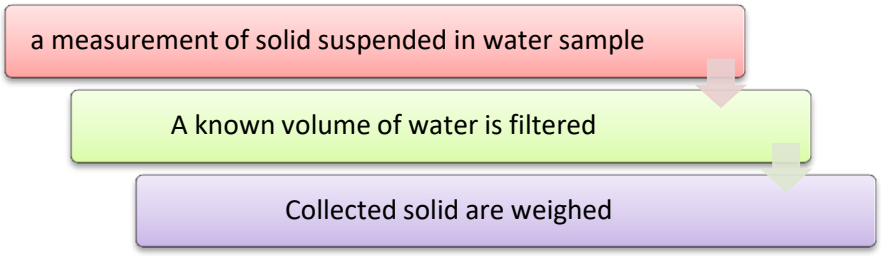
Method used for demasking: Various methods may be used to effect demasking in analytical procedure. These are

1. Decomposition of masking reagent: EDTA may be destroyed by using a strong oxidizing agent such as permanganante in acid medium or simply by digesting with a strong acid.
2. Replacement of the masked ion in a complex by another ion with which the masking agent forms a stronger complex.
3. By change of pH to alter the stability of a complex.
4. By changing the oxidation state of the completed ion.
5. By voltalization of one of the components of the masked system.

GRAVIMETRY

Gravimetry is the process of measuring or weighing a compound or element in a pure form as possible after some form of chemical treatment.

Example



Advantages

1. It is accurate and precise.
2. Possible sources of errors are readily checked.
3. It is absolute method.
4. It is relatively inexpensive.

It is a macroscopic method usually involving relatively large samples. Gravimetric analysis is concerned with weighing of substance that can either be precipitated from solution or volatilized and absorbed.

CLASSIFICATION

Gravimetry may be classified into two major types

- Precipitation Method
- Volatilization Method

PRECIPITATION METHOD –

In this method the analyte is converted into insoluble product and then filtered, washed and heated.

VOLATILIZATION METHOD-

In this method the analyte is heated and analyte and its decomposition product is collected. The resulting loss of mass is determined. When we use thermal or chemical energy to remove a volatile species, this method is known as volatilization gravimetry.

PRINCIPLE:

The principle behind gravimetry analysis is that the mass of an ion in a pure compound can be determined and then used to find the mass percent of the same ion in a known quantity of an impure compound.

STEPS INVOLVED IN GRAVIMETRY

Preparation of the sample solution

↓

Precipitation Process

↓

Digestion of Precipitates

↓

Filteration of Precipitates

↓

Washing of Precipitates

↓

Drying of Precipitate

↓

Ignition

↓

Treatment of Ash

1. PREPARATION OF SAMPLE SOLUTION:

a. Sampling- An ideal sample would be identical in all its properties with the bulk of material which it is taken. The points considered in this step are :

- Cost of test.
- Value of Product.
- End use of Product.
- Accuracy of test method.
- Nature of materials.

b. Dissolution of the sample

Take a clear beaker

↓

Transfer the weighed sample to the beaker

↓

Add sufficient water or alkali to the sample to get clear solution, if heating is necessary

↓

Heat the solution to get clear solution

2. PRECIPITATION PROCESS :

A suitable amount of sample is accurately weighed and dissolved in appropriate solvent to get clear solution. It is then treated with excess of precipitating agent under proper condition to get the precipitates.

Some factors determine the successful analyses of precipitates are as follows.

a. The precipitates must be insoluble.
b. It can be readily separated from solution by filteration.
c. It should be of high purity.

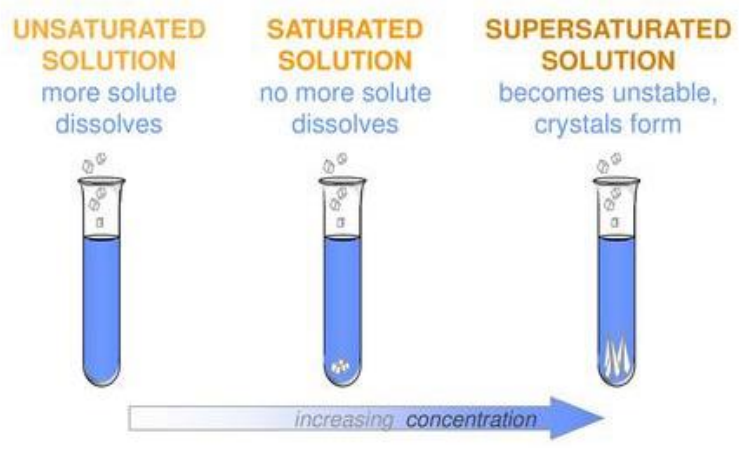
The precipitate formation takes place in 3 steps:

- Supersaturation
- Nucleation
- Precipitate Particle growth.

Supersaturation-

Saturated solution - A solution that contains the maximum amount of solute that is capable of being dissolved. A solution which has the same concentration of a solute as one that is in equilibrium with undissolved solute at specified value of temperature and pressure.

If the solute is added to a solvent with continuous stirring. Firstly solute is dissolved and a stage will come when added solute will not dissolve, but settle at the bottom of the container.



Supersaturated solution - Supersaturated solution contain higher concentration of solute. It contain greater amount of dissolved substance than undissolved substance. This is achieved by heating the saturated solution. This stage appears for short period of time because it is unstable.

Nucleation-

It involves the aggregation of small groups of ions or molecules to form primary nuclei of submicroscopic dimensions. The number of nuclei form depends on the degree of supersaturation.

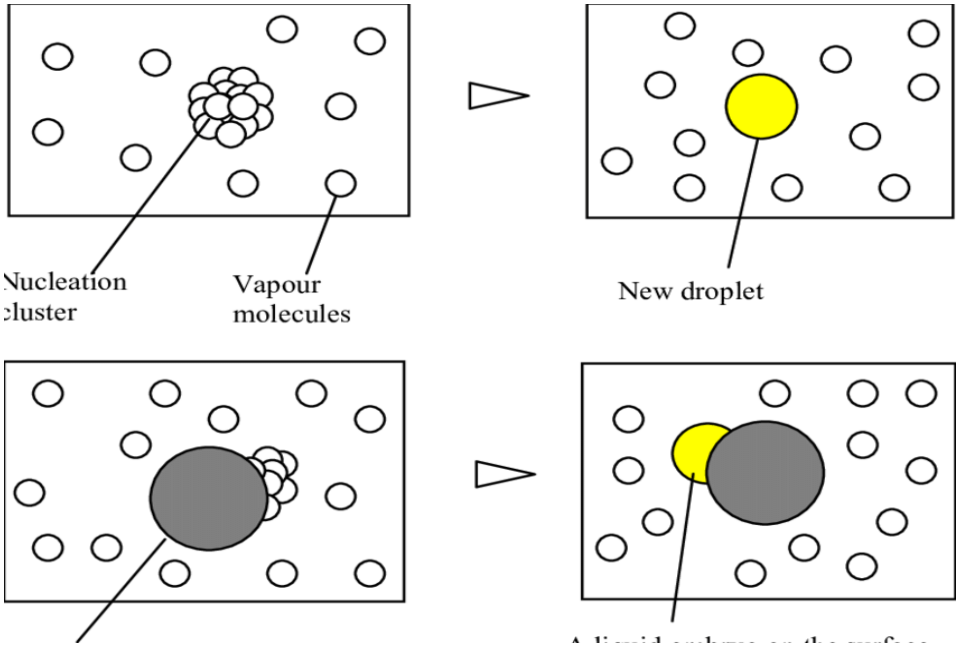
Nucleation

Spontaneous

Ions will join together to form nucleus. It will occurs on its own

Induced

Addition of small solute crystals to supersaturated solution leads to growth of crystals.It requires a seed particle to get things started.



Precipitate Particle growth/Crystal growth-

The particle grows with the addition of ions of the precipitate until the system come to equilibrium. It is achieved after nucleation. It is observed in two cases

- Diffusion of the ions to the surface of growing crystals.
- Deposition of this diffused ion on crystal surface.

The nucleation can be predicted by Von Weimarn Ratio

$$\text{Von Weimarn Ratio} = \frac{(Q-S)}{S}$$

Q- Concentration of reactant before precipitation.

S- Solubility of the precipitate in the medium from it is precipitated.

In order to get particle growth instead of further nucleation we need to make the relative supersaturation ratio as small as possible.

The Physical nature of precipitated particles will be determined by the relative rates of nucleation and particle growth.

When nucleation predominates more number of nuclei are formed small particles are produced and colloidal precipitates consisting of particles within the size range of 10^{-7} - 10^{-5} cm is formed. When particle growth rate predominates coarse precipitates are formed, which are readily collected on filter paper or a filter crucible.

Colloidal State

A substance is said to be in colloidal state if it is dispersed in another medium in the form of very small particle in colloidal state may be between true solution or suspension.

Colloidal solution consisting of following types

1. Dispersed phase- It is also known as discontinuous or inner phase. It consists of discrete particles significantly larger than ordinary molecules but of colloidal size only.

2. Dispersion Medium- It is also known as continous phase or outer phase. It is the medium in which the dispersed phase is present. This consists of continuously interlinked molecules.
3. Stablizing agent- This is substance which tends to keep the colloidal particles apart. Some colloidal are self stabilizer.

Gravimetric analysis encounters situation in which the rate of homogenous nucleation predominates resulting in colloidal precipitates particularly in the initial stage. So, it is necessary to treat such colloidal precipitates to facilitate the filteration.

Some colloidal characteristics include

1. Non settling nature under gravity.
2. Their large surface area.

Example

Electrovalent colloids tend to absorb ions, which are common to them.

In AgCl there will be alternating Ag^{+} and Cl^{-} ions on the surface . The colloids AgCl adsorb either Silver or chloride ion depending on excess availability of Ag or Cl ion during precipitation. This adsorption result in primary layer on surface of colloids particles, which is either positively or negatively charged. The charge of primary layer by a counter layer which carry the opposite charge.

The presence of this primary adsorbed layer and secondary counter ion layer is responsible for stability of colloids. If the secondary layer carrying positive charge than there is electrostatic repulsion in the suspended particle. That does not allow formation of large aggregates and stabilize the colloidal particle/dispersion. Such type of colloidal dispersion does not settle and are difficult to filter.

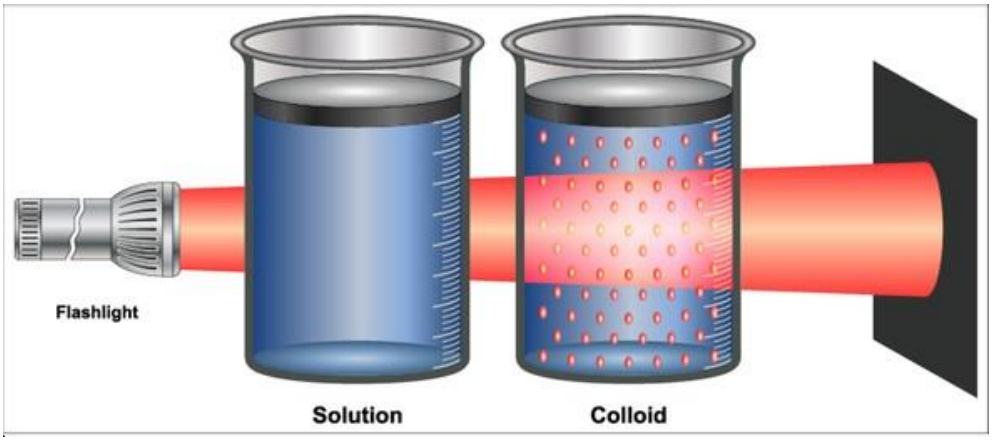
So to make the dispersion unstable the electrolyte can be added with stirring and heating to the dispersion, that neutralize the charge on secondary layer and decrease repulsion between particles and facilitate the binding of individual particle into amorphous mass Which settle down and easy to filter.

The process of conversion of colloidal precipitate into a filterable solid state is said to be **Coagulation or Agglomeration.**

So the analyte forming colloidal suspension is best precipitated from a hot solution containing sufficient electrolyte with constant stirring to yield filterable solid. Some of the factors that affect coagulation are

1. Heating
2. Addition of electrolyte
3. Addition of positive charge

True Solution	Colloidal solution
Carry both positive and negative Charge	Carry only one type of charge
Particle size is smaller than x	Particle size is larger than
It undergoes electrolysis	It undergoes electrophoresis
It undergoes precipitation	It undergoes coagulation, peptization etc
It does not exhibit Tyndall effect	It exhibit Tyndall effect



Conditions of precipitates

- Precipitation carried out in dilute solution.

- Mixing or stirring should be slow and continous that decrease supersaturation and increase degree of large crystal growth.
- The precipitates are affected by hot solution
- The precipitates should be washed with dilute solution of electrolyte.

Contamination of Precipitates.

The sources of contamination of precipitates affecting the gravimetry are

- Post precipitation
- Co-precipitation

Post Precipitation- It involves the deposition of 2nd substance (impurity) on the analyte precipitates when allowed to keep in contact with mother liquor.

Example: Calcium oxalate precipitate out in the presence of magnesium ion satisfactorily without any interference. But if the precipitates remain in contact with mother liquor for long time, then magnesium oxalate precipitates on calcium oxalate. It can be avoided by filtering the precipitates within one or two hours of precipitations.

Co-Precipitation – It involve the inclusion of soluble substance in the precipitates during its formation.

The major types of co-precipitation include:

1. Adsorption
2. Mixed crystal contamination due to isomorphic inclusion.
3. Occlusion.
4. Mechanical entrapment of Non-isomorphic substance.

Adsorption- It depends on surface area of precipitates particle. Colloidal particles with their large surface area adsorb different types of impurities on primary layers.

Mixed crystal contamination- It occurs due to substitution in the precipitate lattice with impurity ion.

Occulsion- It occurs during the formation of precipitate when foreign ion in the counter ion layer gets trapped within the rapidly growing crystals.

Mechanical Entrapment- It occurs when several crystals growing together come closer to each other and trap a portion of solution in pockets between crystals.

Contamination of precipitates can be avoided by **Homogenous precipitation technique.**

Homogenous Precipitation- It is an effective technique in chemical precipitation where the precipitating agents are synthesized inside the solution instead of adding it mechanically. It give filterable dense and relatively pure precipitates.

3.DIGESTION OF PRECIPITATE- The precipitates are left hot for 30 minutes to one hour in order for the particles to be digested. It involves dissolution of small particles and reprecipitate on large one, resulting in particle growth and better precipitation characteristics. This is called as **Ostwald Ripening.**

4.FILTERATION OF PRECIPITATES- Filteration of the precipitates can be carried out using filter papers, sintered glass crucible with porous septum. Filter papers are used to carry out the process of filteration which helps to separate the insoluble precipitate from the mother liquor. Different type of filter paper is used:

• Quantitative Filter Paper: This filter paper is used for the gravimetric analysis has very low ash content. Lower value of ash content is usually achieved by washing with hydrochloric acid and hydrogen fluoride during its manufacturing,

• Whatman Filter Papers : These are generally available with filter paper no. 30, 31, 32, 40, 41, 42, 50, 52, and 54. The no. 42 filter paper is used for very fine particles and no. 41 is used for gelatinous precipitates. The size of the filter paper is based on the bulk of the precipitate and not the volume of the solution to be filtered. The porosity of no. 40, 41 and 42 are 2.4, 2.7 and 3.1 um, respectively.

•Other filter papers used are

- Crucible: A crucible is cup shaped piece of laboratory equipment used to contain chemical compounds heating them to a very high temperature.
- Crucible with Permanent Porous Plates: For precipitates requiring heating up to 2000 C, sintered or glass crucible are used. These are made of resistance glass and

have a porous disc of sintered ground glass fused almost the bottom of the crucible. These crucibles are available in varying porosities for various types of precipitates.

• Crucibles for Ignition of Precipitates in Filter Paper: Types of crucible are used for the ignition of precipitates in filter paper are porcelain and fused silica glass.

• Porcelain crucible can be heated to high temperature (about 1200° C in an oven)

• Fused silica glass crucibles they are widely used as these can withstand very high temperature, even red hot crucible may be immediately dipped in water without breaking, are resistant to most of strong chemical except strong alkali and HF acid.

5. **WASHING OF PRECIPITATES**- It is necessary to wash a gravimetric precipitate as it will be contaminated with non volatile compounds such as the excess of precipitating reagent added. Precipitation of the desired component ions in the presence of one or more soluble compound so it is necessary to remove these as completely as possible by washing. It is important to note that only surface impurities are removed by washing of precipitate. The composition of washing solution will depend on solubility the chemical properties of precipitate and the impurities to be removed. Pure water is not generally used because some of the precipitate may go into solution due to peptization.

Following point must be considered during washing.

- Several washing with small volume of wash liquid are more efficient in removing soluble contaminants than the same total volume used only in one washing.
- Minimum amount of the wash liquid should be used because no precipitate is absolutely insoluble.
- The wash liquid employed for washing must have following properties.
    i. It should not dissolve the precipitate.
    ii. It should not react with precipitate.
    iii. It should not form any volatile or insoluble products with the precipitate.
    iv. It should be easily volatile at room temperature.
    v. It should not contain any substance which is likely to interfere with subsequent determination in filterate.

6. **DRYING OF THE PRECIPITATE:** This may be carried out in an electric oven at 110-125 ^{0}C for few hours. If the ignition is to follow immediately after drying the filter paper, it is dried by keeping the funnel in a current of hot air. The funnel containing the precipitate is first of all covered with a clean perforated paper so that water vapors formed may go out. The flame of the burner is non- luminous and kept low and the burner is then placed to one side of the iron cone to produce only warm atmosphere inside. When the precipitate has dried, it will be separated from the paper easily.
7. **IGNITION AND INCINERATION**: The filter paper having precipitate is taken out of the funnel carefully and opened in such a way that that the finger do not touch the precipitate. Take a dry and clean clock glass and remove as much aapossible of the precipitate on to it. Alternatively, the precipitate may also be collected over a clean and dry glazed paper. Take the help of a feather or camel brush to collect the fine particles of the precipitate. Now cover the precipitate and keep it safe. Fold the filter paper several times so that it looks like a long small cone, Catch the top side of the cone with a pair of tongs by one hand and ignite the cone by mean of flame by the burner in other hand horizontally. Collect the ash in a previously weight crucible placed on a glaze paper. The crucible is then heated strongly to burn off all the carbon to a white ash (may not be white e.g, in case of Fe, Cu etc).
8. **TREATMENT OF THE ASH:** During, ignition the small fraction of the precipitate may get reduced by the carbon of the paper into the compound (or metal) altogether different from the compound in which determination is sought. The ash, therefore is treated with suitable reagents to get back the form (compound) in which it s finally to be weight. This step is called the ash treatment.
For example, crucible is cooled first and then one or two drops of the reagent s added to the crucible and it is evaporated completely by the gentle heating. a second reagent is to be added, the crucible is cooled and then 1-2 drops of this reagent are added and remove as before. The crucible is heated strongly, once again for 5-10 minutes and then cooled. Sometimes the filter paper along with tne precipitate is soaked with the reagent necessary for the ash treatment; it is then dried and charred directly along with the precipitate into the weighted crucible. When the ash treatment is complete, the main bulk of the precipitate from clock into the

crucible. Heat the crucible first gently and then strongly. Cool the crucible first in air, placed on a clay triangle, then in dessicator for 15 min. Now weigh the crucible.

ESTIMATION OF BARIUM SULPHATE

PRINCIPLE: When dilute sulphuric acid is added to dilute solution of barium chloride, a white precipitate of barium sulphate is formed.

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$$

Procedure:

1. Clean and mark three porcelain crucibles, mount at 45° angle and ignite to constant weight.

2. Transfer exactly three 25 mL portions, of the sulfate unknown provided into the 400 mL beakers.

3. Add about 150 mL of distilled water to each sample followed by 5 mL of the HCl solution. Heat to near boiling.

4. Slowly add 25 mL of BaCl, solution with continuous stirring. Continue heating the covered solutions at about 80°C for 1 hour.

5. Filter solutions, while hot, through fine porosity ashless filter paper (Whatman 42 and wash the precipitate with three portions of 10 mL hot distilled water. Check latest filtrate for Cl- by acidifying the filtrate with 2 drops of HNO, followed by 2 drops of $AgNO_3$, If a precipitate is formed, use extra water to wash the precipitate till no precipitate is observed after AgNO3 addition to filtrate portions.

6. Remove the filter papers, fold each one of them and place each in one of the crucibles from Step 1.

7. Heat on a flame to char the paper and then ignite the precipitate on a hot flame till no carbon remains.

8. Transfer the crucibles to a muffle furnace at about 1000°C and ignite the precipitate for 30 min. Remove crucibles into desiccators and weigh after they attain room temperature.

9. Calculate the percentage sulfur in the sample as g S/100 mL.

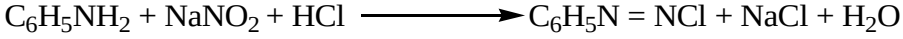
DIAZOTISATION TITRATION

The diazotization titration is nothing but the conversion of the primary aromatic amine to a diazonium compound. This process was first discovered in 1853 and was applied to the synthetic dye industry. The reaction mechanism was first proposed by Peter Griessin. In this method, the primary aromatic amine is reacted with the sodium nitrite in acidic medium to form a diazonium salt. This method is first used in the determination of dyes.

PRINCIPLE

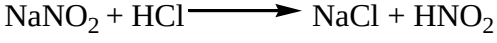
The principle involved in this method is that the primary aromatic amine present in the sample reacts with the sodium nitrite in the presence of acid such as hydrochloric acid to obtain a diazonium salt.The first involved is addition of sodium nitrite to hydrochloric acid cause formation of nitrous acid

Sodium nitrite is added to the solution of amine in the presence of acid at 0–5 °C. The amine reacts with the nitrous acid to form nitrosamine, which is followed by the tautomerisation and the water molecule is lost to form the diazonium ion. This diazonium ion is stabilized by the displacement of the positive charge at the ortho and para positions of the ring.



THEORY

When sodium nitrite is reacted with the hydrochloric acid sodium chloride and nitrous acid are formed



The obtained nitrous acid is reacted with the primary aromatic amine to form the diazonium salt. The excess of nitrous acid is removed by the addition of ammonium sulphamate solution.

$$R - NH2 + HNO_2 \rightarrow R - N = NH + H_2O$$

The end point is detected by the formation of the blue colour with starch iodide paper. This is prepared by immersing the filter paper in the starch mucilage and potassium iodide solution.

$$KI + HCl \rightarrow KCl + HI$$

$$2HI + 2HNO_2 \rightarrow I_2 + 2NO = 2H_2O$$

$$I_2 + \text{starch mucilage} \rightarrow \text{blue colour end point}$$

PROCEDURE

The general procedure is followed by weighing the sample and transferring it into the standard flask. Then concentrated hydrochloric acid and potassium bromide are added and the rest of the volume is filled with the distilled water. This resulting solution is known as the standard solution. The appropriate volume of the standard solution is pipetted out and the temperature is maintained at 0-5 °C. Then the solution is titrated with the sodium nitrite solution until the starch iodide paper turns into blue colour.

Another procedure is—after maintaining the conical flask temperature, the pair of platinum electrodes is immersed. Then the electrodes are connected to the potentiometer and slowly titrated with sodium nitrite solution until a permanent deflection is observed at the end point

END POINT DETECTION

The end point in diazotization titration is detected by the following procedures:

- The excess of nitrous acid is determined by the addition of the starch iodide as an external indicator. After diazotization, one drop of the resulting solution is placed on the starch iodide paper which changes into dark colour.
- Another method for the detection of end point is by immersing the platinum electrodes in the resulting solution and it is also detected by the dead-stop end point method.

- The next method for the detection of the end point in the diazotization titration is by adding the potassium iodide to the nitrous acid with excess acid which liberates the iodine. The liberated iodine is back titrated with the sodium thiosulphate using starch as the external indicator. The end point is detected by appearance of blue colour.
- $KI + HCl \rightarrow HI + KCl$
- $HI + 2HNO_2 \rightarrow I_2 + 2NO + 2H_2O$

Preparation and Standardization of Sodium Nitrite solution

Appropriately weighed sodium nitrite is dissolved in the water and made up to the desired volume.

Standardization of the sodium nitrite is carried out by titrating the previously dried sulphanilamide dissolved in the water and hydrochloric acid solution which is cooled to 15 °C with standard solution of the sodium nitrite.

FACTORS AFFECTING THE DIAZOTIZATION

1. Acid concentration.
2. pH of the $NaNO_2$.
3. Temperature of the reaction (should be maintained at 0–5 °C): the diazonium compounds are decomposed at elevated temperatures.
4. Reaction time (it takes 10–15 min): the compounds react with nitrous acid at different rates based on the nature of the compound.
5. Slow diazotizable groups: sulpha groups, carboxylic groups and nitrogen oxide group.
6. Fast diazotizing groups: anilide, toluidine and aminophenol.

Conditions for diazotization titration

The following conditions are required for the diazotization titration of the amino group containing samples. They are as follows:

1. Rate of titration: Addition of sodium nitrite to the sample solution takes time to react with the amino group present in the sample solution. Different amino compounds react with the nitrous acid at different rates. Based on this, the amino compounds are classified into two main groups. They are as follows:
    1. Slow diazotizable compounds
    2. Example: Sulphanilic acid and anthranilic acid
    3. Fast diazotizable compounds
    4. Example: Aniline, aminophenol, and toluidine

5. The reaction rate is increased by the addition of the potassium bromide solution.

2. Temperature: Maintenance of the temperature is the main condition for the diazotization titration. The diazonium salts formed are not stable at elevated temperatures. They are readily decomposable at elevated temperatures, therefore, the temperature should be maintained at 0–5 °C.

TYPES OF DIAZOTIZATION TITRATION

There are mainly three types of methods based on the titration procedure. They are as follows:

1. Direct method: The main principle involved in this method is to treat the amino group containing drug with the acid solution. The resulting solution is immersed in the cold water bath or ice water bath by maintaining the temperature at 0–5 °C. Then this solution is titrated with the sodium nitrite solution. The end point is determined by the above-mentioned methods.
2. Indirect method: The principle involved in this method is that the excess nitrous acid is added to the titration sample solution and it is back titrated with the other appropriate titrant. This method is mainly used for the titration of insoluble diazonium salts.
3. Other method: The main principle involved in this method is the formation of the diazo oxide which is more stable than the diazo compounds. For example, the aminophenol is readily oxidized by the nitrous acid and converted to the quinones in the presence of copper sulphate solution and forms the diazo oxide compounds. This readily undergoes the coupling reaction with the nitrous acid.

ADVANTAGES

- Selective for the all types of sulphonamides.
- Sensitive
- Reproducibility

DISADVANTAGES

- Applicable for a very less variety of samples.
- Relatively slow when compared to other methods.
- Temperature conditions to be properly maintained throughout the reaction.
- The end point detection is very difficult.

- The colour produced is not stable.
- Lack of specificity.

APPLICATIONS

- Used in the determination of the sulphonamides.
- Method: An accurately weighed 1 mg sample of sulphonamide is dissolved in the 4 ml of concentrated HCl and in 10 ml of distilled water. Then, this solution is cooled to 15 °C and titrated with the 0.1 M of sodium nitrite solution. The end point is determined by streaking one drop of the titration solution on the starch iodide paper until blue colour is appeared. The percentage amount of the sulpha drug is determined by the following equation:

$$\text{Percentage of sulpha drug} = \frac{V \times M \times EW}{W \times 10}$$

- where V is the volume of the titrant consumed; M is the molarity of the titrant; EW is the equivalent weight of the drug; W is the weight of the sample.
- Used in the determination of the chloropheneramine.
- Method: The accurately weighed sample is added to the 5 ml of HCl and 50 ml of distilled water. Then the solution is cooled to 15 °C. Then the solution is slowly titrated with the 0.1 N sodium nitrite solution using starch iodide paper as the indicator.
- Used in the determination of the dopamine.
- Used in the determination of the procaine.
- Used in the determination of the amphetamine.
- Used in the determination of the procaine
- Used in the determination of the ephedrine.
- Used in the determination of the P-amino benzoic acid (vitamin B4).
- Method: The accurately weighed sample is added to the 5 ml of HCl and 50 ml of distilled water. Then the solution is cooled to 15 °C. Then the solution is slowly titrated with the 0.1 N sodium nitrite solution using starch iodide paper as the indicator.
- 1 ml of 0.1 N sodium nitrite ≡ 0.01371 g of vitamin B4

IMPORTANT QUESTIONS

Very short Questions

1. Define solubility product?
2. What is salt effect?
3. What are the conditions required for precipitation titrations?
4. What is the effect of temperature on the solubility of precipitates?
5. Define fractional precipitation.
6. What are argentometric titrations?
7. What is the effect of common ion on the solubility of precipitates?
8. Explain Fajan method for precipitation titrations.
9. What are indicators?
10. Name different types of indicators used in precipitation titrations.
11. What are adsorption indicators? Give examples.
12. What are Mercuric Nitrate titrations?
13. How solubility products affect the amount of precipitation?
14. What are potassium chromate and ferric ammonium sulphate indicators?
15. What is gravimetric analysis?
16. What is digestion of precipitate and why it is necessary?
17. Define supersaturation.
18. What are colloidal solutions?
19. What is coagulation value?
20. What do you mean by term colloidal state?
21. What is Saturated solution?
22. What do you mean by term colloidal state?
23. Define fractional precipitation?
24. What are organic precipitants.
25. Define Peptization.
26. What is von weimarn ratio

Short Answer Questions

1. What is precipitation titration?
2. Classify precipitation titration according to determine the end point detection.
3. Give any two requirements for the precipitation titration.
4. How will you standardize 0.1N AgNO3 solution.
5. What is the role of acetic acid and methanol in the standardization of 0.1 N AgNO3 solution.
6. What is the use of nitrobenzene or dibutylphthalate in modified Volhard's method.
7. What are adsorption indicators? Give some examples.
8. What is Complexometric titration?
9. What are Ligands?
10. What is chelate?
11. What is pH and pM indicator? Give examples.
12. Define masking and demasking agents.
13. Add a note on stability of complexes.
14. Explain the different types of Complexometric titration.
15. Write a short note on pM indicators and it's classification.
16. Describe the role of masking and demasking agents in Complexometric titration.

Long Answer Questions

1. Write the principle and procedure involved in the assay of Sodium chloride by Mohr'smethod.
2. Give briefly about the Fajan's method in precipitation titration.
3. Explain the determination of halogens and thiocyanates by Volhard's method.
4. Compare the advantage and disadvantage of precipitation titration methods.
5. Explain the theory involved in the complex formation.
6. Explain the types of Coprecipitation
7. Explain estimation of Barium sulphate.
8. What is the principle involved in the diazotization titrimetry?
9. what are the conditions required for the diazotization titrimetry?

10. What are the example drugs assayed by the diazotization titrimetry?
11. What are the advantages of diazotization titrimetry?
12. What are the factors that affect the diazotization end point?
13. What are the different methods used for the end point detection in the diazotization titrimetry?

MCQ

1 Which analytical method is based on the weight of the PPT ?

A. Acid base Titration

B. Complexometric Titration

C. Precipitation titration

D. **Gravimetry**

2. Gravimetric analysis involve conversion of analyte into

A. Formation of precipitate occurs

B. Formation of insoluble substance occurs

C. **Both A and B**

D.Formation of Soluble salt occurs

3. Gravimetric analysis is type of…… analysis

A. Qualitative

B. **Quantitative**

C. Volumetric

D.Titrimetric

4. If impurity is adsorbed on surface of precipitate, it is an example of

A. Co-precipitation

B. Surface adsorption

C. **Both A and B**

D.Occlusion

5. If solution contains more of the dissolved salt than it could be dissolved under normal circumstances, it is called as

A.Saturation

B. **Supersaturation**

C. Nucleation

D.Precipitation

6. **Which is the correct sequence of steps in gravimetric analysis**

A.Filteration, Digestion, Washing

B. Digestion, Washing, Filteration

C. Washing, Digestion, Filteration

D.**Digestion, Filteration, Washing**

7. Which one is favourable condition for precipitation

A. It should be carried out in dilute solution

B. Reagent should be mixed slowly with constant stirring

C. It should be carried out by using hot solution

D.**All are correct**

8. **During post precipitation**

A. Impurity is trapped in crystal

B. **Second substance slowly precipitate**

C. Impurity is adsorbed on surface

D.None of these

9. Pure water is not used as wash liquid because it carry out

A. Co-precipitation

B. Post-precipitation

C. **Peptization**

D. Coagulation

10. Which is not requirement of wash liquid

A. It should not dissolve precipitate

B. It should dissolve impurities

C. **It should carry out peptization**

D. It should be easily evaporated

11. Drying is the process of removalof

A. **Solvent water**

B. Occlude water

C. Adsorbed water

D. Water crystallization

12. Digestion is also called as

A. **Ostwald ripening**

B. Co-preciptation

C. Coagulation

D. Water crystallization

13. Which method are used to determination of primary amine ?

A. **Diazotization Titration**

B. Karl fischer titration

C. OFC

D. All of the above

13. Which temperature Is required to be performing Diazotization reaction ?

A. 25 to 30^0C

B. 0 to 5^0C

C. 10 to 15^0C

D. All of the above

14. Which method is used to determination of end point of Diazotization Titration ?

A. Starch iodine paper

B. Potentiometric titration

C. A and B

D. None of the above

15. Diazotisation is explained as

A. Reaction between primary aromatic amine and Nitrous acid.

B. Reaction between cyanoand nitric acid.

C. Reaction between dibasic amine and acid.

D. Recation between 920 compounds and HCl.

16. Formula of Diazonium salt

A. ArN_3X

B. ArN_2X

C. CNH_2.

D. CH_3 NH

17. Diazotisation is method to determine

A. Primary Aromatic amine

B. Secondary Armatic amine

C. Primary aliphatic amines .

D. None of the Above.