General Principles of chemical analysis

- What is Chemistry? Or what you know about chemistry?
- Chemistry is branch of science that deals with the study of matter w.r.t. composition, structure properties & its uses
- Organic Chemistry: The study of the structure, preparation, properties, and reactions of carbon compounds
- Inorganic Chemistry: The study of chemical reactions and properties of all the elements and their compounds, with the exception of hydrocarbons, and usually including carbides, oxides of carbon, metallic carbonates, carbon-sulfur compounds, and carbon-nitrogen compounds
- Physical Chemistry: study of interrelationship between matter & energy
- The branch of chemistry that deals with the interpretation of chemical phenomena and properties in terms of the underlying physical processes, and with the development of techniques for their investigation
- Analytical Chemistry: To find out what a substance is composed of and exactly how much
- The branch of chemistry dealing with techniques which yield any type of information about chemical systems
- What is engineering: Applications of basic sciences
- What is Technologist? : Improvements in used materials for more sophistication

Analytical Chemistry

- This is combination of two words Analytical and Chemistry
- Analytical coming from Analysis
- This is very important problem solving tool (technique)
- Hence it is one kind of art i.e people with this art can solve their daily problems with ease Thus
- Techniques which yield any type of information about chemical systems.
- Analytical chemistry is Art & Science of determination of composition of mixture qualitatively & quantitatively.   i.e. to find out what a substance is composed of and exactly how much.
- **Why we performs chemical analysis ?/ Purposes of performing chemical analysis**
- 1.To know exact quality of substance in terms of component/ ingredients present in it
- 2.To know exact composition of all ingredients in given substance/ required ingredients
- 3.Identifying unknown substances 4.Separation of ingredients 5.For determining structures
- This is possible with or without instrument depends on situation of sample & requirements

CHEMICAL ANALYSIS

- *Definition: Resolution of a chemical substances/ material into its proximate or ultimate parts*
- Different types of chemical analysis may be classified as follows
- **On the Basis of purpose of analysis, there are two types**
- 1. Proximate (Qualitative): What no of constituents are present and not it's amount i.e identification of ingredients
- 2. Ultimate(Quantitative): Exact contribution of each element irrespective of composition
- **On the basis of objective of quantitative analysis, there are three types**.
- 1. Complete analysis: Here contribution/ proportion of each constituent is estimated e.g. coal analysis %C,%H,%N,%S,%O Possible by vol. gra. Instrument etc
- 2. Partial: Here only required/ specific/ selected element or ingredient/component in the sample is estimated: e.g. in alloy of brass % of Zn estimation, In Carbon steel % of Carbon estimation etc Possible by vol. gra. Instrument etc
- 3. Trace: Here determination of trace constituent present in the sample estimated: e.g In water analysis estimation of carcinogenic constituent such as Pb, Hg etc. which are present in trace amount Possible by Instrument
- **On the basis of size of sample there are 5 types of quantitative analysis**
- 1.Macro: size/ quantity of sample > 0.1 gm
- 2.Meso (semi micro) : size/ quantity of sample between 10^{-1} to 10^{-2}--- 0.1 to 0.01 gm
- 3.Micro: size/ quantity of sample between 10^{-2} to 10^{-3} 0.01 to 0.001gm
- 4.Sub micro: size/ quantity of sample between 10^{-3} to 10^{-4} 0.001 to 0.0001 gm
- 5.Ultra micro: size/ quantity of sample below 10^{-4} gm
- **On the basis of Method used for chemical analysis, there are two types**
- 1.Qualitative & 2.Quantitative analysis
- Qualitative of two types 1Semi Qualitative 2.Organic spotting
  There are two Types of Quantitative Analysis
1. Non Instrumental methods of analysis. This is also called Classical method of analysis
   There are two types : 1.Volumetry & 2. Gravimetry

<u>a) Volumetry:</u> Quantiative analysis involving determination of quantity of analyte in terms of volume of standard reagent reacted chemically with it.

On the basis of chemical reaction taking place during it they are further classified as

1. Neutralization/ Acid –Base titration
2. Redox/ Oxidation- Reduction Titration
3. Iodometric titration
4. Precipitation Titration
5. Complexometric titration

<u>b)Gavimetry</u>: This is quantitative analysis involves, determination of ion/ element/ component/ingredients by accurately weighing it into desirable compound having definite chemical composition.

2. <u>Instrumental methods of analysis</u>. Here Quantity of analyte measured by measurement of appropriate electrical properties (potentiometer) or measurement of optical properties (absorption/ emission/ transmittion spectra) in some cases measurement of combination of electric and optical (amperometric titration)

<u>Electrical method of analysis</u>: i) Voltammetry: measurement of current at a micro electrode at a specific voltage
2.Coulometry: : measurement of current and time needed to complete an electrochemical reaction
3. Potentiometry: measurement of potential of an electrode in equilibrium with an ion to be determine
4. Conductimetry: measurement of the electrical conductivity of a solution

<u>Optical method of analysis:</u> 1. Measurement of the amount of radiant energy of a particular wavelength absorbed by the sample 2. Emission of radient energy emitted 3.Absorption may be Visible/ UV and IR spectroscopy. On the basis of amount of light stopped or scattered by a suspended particles Turbidimetric and Nephelometric analysis. Instrument like pH Meter Colorimeter/Spectrophotometer Conductometer, UV,IR,NMR, Mass, Chromatography, etc

<u>Quantitative:</u> 1. Flame photometry: Used in inorganic chemistry to determine the conc. Of metal ion
2. AAS: Atomic absorption spectroscopy: Determine metal elements using absorption of optical radiation by free atom in gaseous state.
3. UV-Visible spectroscopy: Measured absorption of light in visible region.
4. EDAX: Energy dispersive X-ray : used for elemental analysis from X ray emitted by the matter in response to being hit with the EMR.

<u>Structure:</u> 1.IR: Change in vibrational energy leads change in the dipole moment between atoms of molecule.
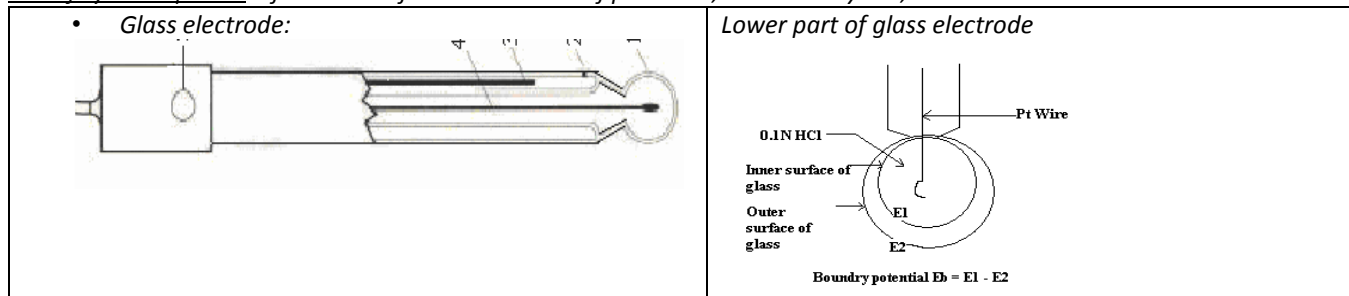2. NMR: Many nuclei having spin & all nuclei are electrically charged if external magnetic field is applied energy transfer is possible between the base energy to a high energy level.

<u>Structure Solid</u>: X ray Diffraction

<u>Separation from complex mixture</u>: Chromatography

<u>Study of Surface morphology by microscope:</u> 1. SEM(Scanning electron Microscope) Electron beam interact with sample producing secondery electron, back scattered electron, Auger electrons and can be converted to surface tropograpy image.
2. TEM(Transmission electron Microscopy) When beam of electron passing through thin specimen electron are scattred after interaction with atom. It is used to study the growth of layer, composition and defects in semiconductors.
3. AFM (Atomic force Microscope) Cantilever/ Tip assembly scan the surface.

<u>*Out of Syllabus point :*</u> *Information of Glass electrode of pH meter, Conductivity cell, colorimeter*

• *Glass electrode:*	*Lower part of glass electrode*

Pt Wire
0.1N HCl
Inner surface of glass
Outer surface of glass
E1
E2
Boundry potential Eb = E1 - E2

• *Working: Glass electrode: Lower bulb of glass electrode is highly sensitive to H^+ ion concentration. It is made up of 22% Na_2O, 6% CaO, and 72% SiO_2. Thickness of this glass varying from 0.001 – 0.05 mm. It possesses low M.P. & high electrical conductivity. Therefore ordinary potentiometer is not used to detect pH of low strength solutions. It is represented as Pt or Ag/ AgCl / 0.1 N HCl / Glass bulb/ Test solution.*
• *When glass electrode immersed in unknown solution, due to variation in concentration of H^+ ions inside & out side of the bulb potential is develop on inner & outer wall of glass bulb due to exchange of H^+ & free Na^+ present in crystal*

lattice of glass bulb, denoted by E1 & E2 potential. Difference between this two potential is called boundary potential. This potential is sanded to one of the terminal of potentiometer, while other terminal is connected to reference electrode. The potential is measured. In pH meter this potential is directly converted to pH units, we get direct pH of any solution
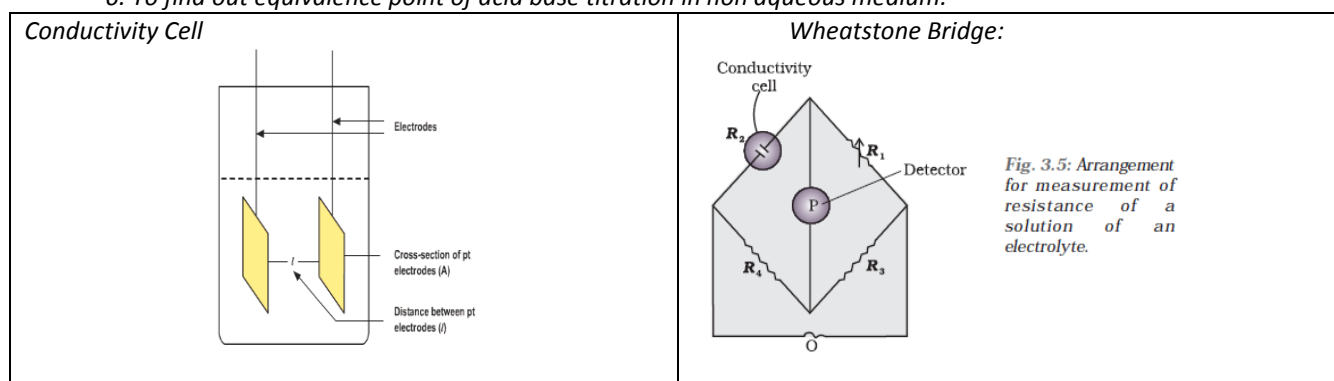
Advantages Of glass electrode
- *1 It is most convenient & simple to use   2. It is not easily poisoned 3. Equilibrium is rapidly achieved*
- *4. The results are accurate 5. It has no salt or protein error 6. It can be used in turbid, colored & colloidal solutions. 7. pH measurement is possible even with few milliliters of solution 8. It can be used both in alkaline & oxidizing solution*

DisAdvantages Of glass electrode
- *1. It is fragile & used with great care 2. As the glass membrane has a very high electrical resistance the ordinary potentiometer can't be used for measurement 3. Standardization has to be carried out frequently*
- *4. It doesn't work in dehydrating solutions like ethyl alcohol, acetic acid & gelatin*
- *5. Ordinary glass electrode works up to 9 pH & special kind of electrode work up to 13 pH*

Applications of pH metry
- *1. Equivalent point of any type of Acid – Base titrations*
- *2. To carry out above titrations in presence of strong oxidant, reductants, viscous protein mediums, as well as colored, colloidal, complex, poisonous solutions.*
- *3. To carry out weak acid weak base titrations or for dilute solutions. 4. To carry out equivalent point of mixtures of two or more acids or bases in single titration.*
- *5. To find out equivalence point of di & tri basic or acidic substances in single titrations.*
- *6. To find out equivalence point of acid base titration in non aqueous medium.*

Conductivity Cell	Wheatstone Bridge:
	Fig. 3.5: Arrangement for measurement of resistance of a solution of an electrolyte.

Applications of conductometer
- *1. Colored solutions which cannot be titrated by ordinary volumetric method with the help of indicators can be successfully titrated conductometrically.*
- *2. The method can also be employed in the case of very diluted solutions & also for weak acid & bases.*
- *3. No special care is necessary near the end point as it is determined graphically*

Ray diagram Colorimeter:

Ray diadram for colorimeter
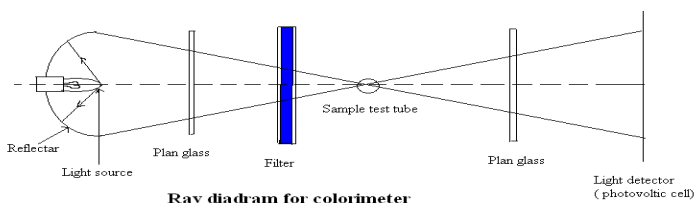
- *The working of colorimeter/ Spectrometrically is based on Beer's- Lambert's law. It state that, When beam of monochromatic light passing throw homogeneous absorbing medium, decrease in intensity of light is directly proportional to intensity of incident light as well as concentration of absorbing medium*
- *Transmission Or Transmittance: (T): It is simple ratio of intensity of transmitted light to incident light*
- *i.e. $T = It / Io$*
- *Optical density (OD) or Absorbance (A): It is simple logarithmic ratio of intensity of incident light to transmitted light. OD or A = log Io/It*

Volumetric analysis

- Quantiative analysis involving determination of quantity of analyte in terms of volume of standard reagent reacted chemically with it.
- Basic principle of this analysis based on following reaction.

  $a A + t T \rightarrow$ Product
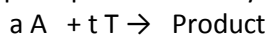
  Where 'a' is molecules of analyte A

  ' t ' is molecules of reagent T

- Quantiative analysis involving determination of analyte in terms of volume of standard reagent reacted chemically with it. or
- It is type of quantitative analysis (chemical)in which amount of analyte is determined in terms of volume of standard solution of suitable substance
- E.g. 1L 1N $KMnO_4$ = 52 gm of Fe
- **Terminology in volumetry**
- Titration: Process of adding titrant in titrand till chemical reaction between them completed
- Titrant: The reagent of known concentration i.e. standard solution used during titrimetry is called titrant.
- Titrand: The substance being titrated i.e. sample under test is called titrand
- Indicator: Auxillery Substance added during titration which indicates termination of reaction by physical change i.e coluor,ppt etc is called indicator.
- Equivalence point:
- This is a stage in titration at which the titrant &titrand is chemically equivalence is called equivalence point
- Theoretical end point: This is a stage in titration at which the reaction between titrant &titrand is just completed is called
- Stoichiometric End Point: This is a stage in titration at which the titrant &titrand is stoichiometrically equivalence is called Stoichiometric point
- Practical end point/End point: Point in titration at which, indicator show physical change in solution visible to analyser is called end point or visual end point or practical end point
- Titration error: The difference between theoretical & practical end point is called titration error
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    Advantages of Non Instrumental methods over Instrumental methods
    1. Procedures are rather simple and accurate. 2. Methods are based on absolute measurements.
    3. No need of special training as such. 4. Required apparatus are easy to available with low cost.
    Disadvantages of Non Instrumental methods over Instrumental methods
    1. Procedures are time consuming. 2. Some time chemical conditions are very critical.
    3. Colored, Colloidal, Complex, Diluted & Poisonous samples cannot estimated.
    4. Accuracy of result decreases with decreasing sample under test
    Advantages of Instrumental methods over Non Instrumental methods
     i) They are highly sensitive ii) Colored, Colloidal, Poisonous & complex sample can be handled with ease
     iii) Small amount of sample can be easily detected iv) Time saving analysis
     v) Measurements are more accurate & reliable.
    Disadvantages of Instrumental methods over Volumetry
    i) Before analysis, Calibration of instrument is required ii) Initial cost & maintenance cost required is high
    iii) Special training as such is required iv) Accuracy & reliability of result depends on reference used for their calibration v) Clean & sizable space is required vi) Limits of Concentrations is always their. (Permissive & Excessive limits of concentration of each instrument)

Standards

- Definition: Standards are chemical substances used in the form of standard solution which undergo chemical reaction with analyte
- Classification: They are classified on the basis of its purity as Primary standards & Secondary standards

Primary standards

- Definition: These are substance used in chemical analysis,which are extremely /high purity & not affected by any type of weathering conditions. Hence used directly to prepare their standard solutions called primary standards OR These are chemical substance, used direly to prepare standard solution.
  Apart from purity other Characteristics of primary standards
  Beside purity primary standards must fulfill following requirements
1. Availability: It should be easily available in pure & dry form at a reasonable cost
2. Stability: It should be stable i.e. easy to dry (not hygroscopic)i.e. They should not lose weight on expose to air while weighting. Or if unstable, they looses their purity & become sec. std i.e It cannot weighted with fixed amount which is characteristic of primary standard.
3. Molecular weight : It must Bear high Molecular Weight. This parameter important while preparing very dilute solution e.g. 0.01N, 0.001N etc. In case of high concentrated solution weight of primary standard required must be weighted errorless.Hence High mole.wt. ensure errorless weighing while preparing dilute solution.
   e.g. LiOH 26 & EDTA 336 (If mol.wt. is low, small amount of sub. Cannot be weighted accurately)
4. Solubility: Readily soluble in common or available solvent

5. Purification: Highly pure if impure can be purified by simple purification method like evaporation.
6. Reactivity: Completely react with analyte through stoichiometric reaction. Rate of reaction can be increased by stirring or by catalyst.

Acids: Potassium hydrogen phthalate.
C_6H_4 (COOK)(COOH), Benzoic acid C_6H_5COOH, Constant boiling HCl

- Bases: Sodium carbonate Na_2CO_3, Mercuric oxide HgO, Borax $Na_2B_4O_7$
- Oxidizing agents: Potassium dichromate $K_2Cr_2O_7$, Potassium bromate $KBrO_3$, Potassium iodite KIO_3,
- Reducing agents: Sodium Oxalate $Na_2C_2O_4$, Arsanious Oxide As_2O_3, (KI)Iodine I_2
- Others: NaCl, KCl

Secondary standards

- Definition: These are the chemical substances used in the form of solution, only after standardization by suitable standard solutions
- i.e solution prepared by dissolving a known wt to get definite volume of solution is not directly used as burette reagent unless its standardization
  Example: NaOH hygroscopic, low purity
- Acids: HCl, HNO_3, $HClO_4$,Sulphamic acid (HSO_3NH_2)
- Bases: NaOH,KOH
- Reducing agents: $Na_2S_2O_3$, $KMnO_4$

Comparison between primary and secondary standards

Primary	Secondary
Available always with High purity	Not always available high purity
Stable in all types of Weathering conditions	May or May not stable Weathering conditions
Can be purified by simple Means	Cant purified by simple Means
Used directly to prepare Standard solution	Used only after std with std. solution
e.g Constant boiling HCl etc	e.g. HCl, NaOH etc

CONCENTRATIONS OF SOLUTIONS

Terminology in Concentration:
- Solution: A homogeneous mixture of two or more different ingredients which are evenly distributed in each other OR A homogeneous mixture of two or more different ingredients which are present on molecular level OR A homogeneous mixture of two or more different ingredients which are uniformly distributed
- OR A homogeneous mixture of two or more different ingredients which are forming single phase
- Solute: A component of solution present in lesser proportion/minor proportion.
- Solvent: A component of solution present Greater proportion/major proportion.
- Dilute solution: Solution containing negligible amount of solute w.r.t. solvent
- Concentrated solution: Solution containing considerable amount of solute w.r.t. solvent
- Saturated solution: Solution containing maximum possible amount of solute w.r.t. solvent
- Conc. In % term: Amt of solute in term of direct % compared to mass/ volume of solution e.g. ppm/ mg/lit etc.
- Conc. of solution: Amount of solute per unit mass/ volume of solution
- 1. Conc expressed in molar term: It uses amount of solute as no.of moles
- Molar concentration: Amount of solute is measured as no. of moles of solute
- Moles of solute: Amont of solute equal to its mole.wt. in gm
- No.of moles of solute= Act.wt. of solute/Mo.wt of solute   i.e. n = W/M
- Molarity (M): Number of mole of solute present in one liter of solution is called Molarity.

$$Molarity = \frac{Number\ of\ mole\ of\ solute}{Volume\ of\ solution\ in\ liters}$$

- e.g. 0.1 M KCl is prepared by dissolving 7.45 gm of it in 1 liter water

Molality (m): Number of mole of solute present in per kilogram of solvent is called Molality.

$$Molarity = \frac{Number\ of\ mole\ of\ solute}{Weight\ of\ solvent\ in\ kilograms}$$

- e.g. 0.1 m KCl is prepared by dissolving 7.45 gm of it in 1 Kg of water
- Conc expressed in Normal terms
- It uses amount of solute as no of gm equivalence wt.
- <u>Gr. Eq. wt.:</u> Amount of solute equals to its Eq. wt in gm
- <u>Normal conc.</u>: Amount of solute is measured as no. of gm. Equivalent of solute
- <u>No. of gm Eq. wt (e)</u> = Actual wt of solute/ Its Eq. wt i.e. e= W/E

  <u>Normality (N):</u> Number of gram equivalent of solute present in one liter of solution is called Normality.

$$Normality = \frac{Number\ of\ gram\ equivalent\ of\ solute}{Volume\ of\ solution\ in\ liters}$$

- e.g. When 5.6 gm of KOH is dissolved in 1 liter of water prepared solution is 0.1 N
- When 9.8 gm of H_2SO_4 is dissolved in water up 1 liter prepared solution is 0.05 N

• Expression of concentration during titrimetry

- During titrimetric analysis expressing conc of std. solution is decided on the basis of types of chemical reaction and stoichiometry
- 1. During titration If N=M for T & D, concentration expressed either Normal or Molar term
- E.g . May be either molar or normal term HCl + NaOH   NaCl + H2O
- During titration If N not equal to M for T & D, concentration expressed in Normal term only
- E.g H2SO4+2NaOH   Na2SO4 +2H20
- When complexing agent react with metal ions, it is always expressed in terms of mole.
- E.g EDTA + Ca   CaEDTA

Desire requirements of standard solutions

- Following are desire requirements of standard solutions
- 1.Have long term stability in solvent 2. React rapidly with the analyte 3. React completely with analyte
- 4. Be selective to the analyte

Numerical on Concentrations

- **1.Calculate the molarity of a solution of KOH if 11% KOH is prepared (Mo. Wt. 56)**
- Solution: 11% by w/v means 11gm in 100ml solution.
- M=n/V, n= W/Mol.wt, & V = 100/1000
- M= 11/56 X 1000/100 = 1.964M
- **2. How much $(NH_4)_2SO_4$ is req. to prepare 400cc of M/4 solution (132.1)**
- Amt of $(NH_4)_2SO_4$ req = Strength X Mol. Wt X vol. of solution in Lit
-                   = ¼ X 132.1 X 400/1000   = 13.21gm
- **3. How many gm Equivalence are contain in a) 1 L of 2N soln. b) 1 L 0.5N soln. c) 0.5 L 0.02N soln.**
- 2gm, 0.5gm, 0.1gm equivalence
- **4. What is molarity of a solution containing 20gm Cane sugar in 125 gm DW**
- ($C_{12}H_{22}O_{11}$=342)
- n = 20/342 & V = 125/1000, M = 0.468
- **5.Calculate normality of each of following a) 7.88gm HNO_3/lit & 26.5gm Na_2CO_3/lit (MW63& 106)**
- a) 7.88/63 = 0.12N & b) 26.5/53 = 0.5N
- **6. The molarity of a solution of ethanol (C_2H_5OH) is 3.6M at 25^{0}C. Calculate the molality of a solution.**
  Density= 0.95gm/cc
- 1 Lit C_2H_5OH = 950gm, 950gm soln. contains 3.6M C_2H_5OH, Thus wt of C_2H_5OH in 950 gm sol = 46X3.6 = 165.5 gm, Hence wt of solvent = 950 – 165.5 = 784.4gm
- Therfore m = 3.6/0.7844 = 4.5895 m
- **7.How many gms of 5% by wt NaCl is required to get 3.2gm NaCl.**
- 5% means 5gm in 100ml soln., for 3.2gm soln req = 3.2 X 100/5 = 64ml
- **8. How many cc of 2M Pb(NO3)2 will conatin 600mg of Pb (MW pb =208.5, Pb(NO3)2 = 331.2)**
- 2M Pb(NO3)2 = 662.4 gm/lit = 417gm/lit only Pb, Therfore 1 ml soln = 417mg of Pb, Therefore 0.6gm of Pb = 0.6/0.417 = 1.4388ml solution
- **9.Calculate molarity,Normality of 29.5% H2SO4(v/v) having density 1.216gm/cc (MW98.08)**
- Wt of 29.5% H2SO4 = 29.5 X 1.216 = 35.872 ∆ n = W/M = 35.872/98.08 = 0.3657
- TF M = n/ Vol.in Lit = 0.3657/100 X1000 = 3.0657M,
- M = 3.0657/ (1.216-0.3587) = 4.266m
- **10. Calculate purity of Conc H2SO4 (1.8gm/cc) if 5ml of it is neutralized by 84.6 ml of 2N NaOH**

- 1N 1L NaOH = 40gm, 84.6ml 2N NaOH = 6.768gm TF Eq. of NaOH = 6.768/40 = 0.1692, Henc Eq of H2SO$ = 1.692 X 49.04 = 8.2975, Density of H2SO4 is 1.8 TF wt of 5ml of H2SO4 is 9 gm TF Purity = 8.297 X 100/ 9 = 92.05
- **11.Compute the volume of Conc. HNO3 having density 1.112gm/cc & containing 63% acid required to prepared 15 Lit of 0.125N solution (MW 63)**
- Normality = 1112 X 0.63 / 63 = 11.22N
- N1V1 =N2V2, 11.12 X V1 = 15 X 0.125 = 0.168615Lit
- **12.How many kg of wet NaOH containing 12% H_2O are requied to prepare 60 L of 0.5 N solution**
- 1L 0.5 N NaOH solution= 0.5 X 40 = 20 gm thus 60 L 0.5 N = 20 X 60 = 1200gm = 1.2 Kg
- Now 1 Kg pure NaOH = 100/88 Kg of 12% wet NaOH thus 1.2 X 100/88 = 1.36Kg of 12% wet NaOH required
- **13.Given the unbalanced equation**
- **$KMnO_4 + KI + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + I_2 + H_2O$**
- **How many gram KMnO4 is needed to make 500cc 0.25N solution**
- **How many gm KI is needed to make 25 cc of 0.36N solution**
- In this reaction OS of Mn changes from +7 to +2 hence eq. wt is = 158/5 = 31.6 gm
- Hence Wt. required = 0.5 X 0.25 X 31.6 = 3.95gm is required
- In this OS , Iodine changes from -1 to 0 hence mole.wt = eq. wt
- Hence weight req = 0.025 X 0.36 X 166 = 1.49gm
- **14.To what extent must a 0.5M BaCl2 solution be diluted to yield 20 mg Ba++/CC (Ba-137.3)**
- Original solution contain 0.5 mole Ba++/L i.e 137.3/2 = 68.6 mg/cc
- C1V1 =C2V2, 1X 68.6/20 = 3.43 i.e each CC of OS diluted to 3.43 cc then each CC = 20mg of Ba++
  15.Exact 4 gm solution of H_2SO_4 was diluted and excess of $BaCl_2$ is added. The dried ppt of $BaSO_4$ weighted 4.08gm. Find % of H_2SO_4 in original solution. (Mole wt H_2SO_4 = 98.08, $BaSO_4$ = 233.4)
  Mass of H2SO4 to get 4.08gm BaSO4
- H2SO4 + BaCl2 → BaSO4 + 2HCl
- =(4.08/233.4)X 98.08 = 1.72gm
- H2SO4 by weight = Mass of H2SO4/Mass of solution = 1.72/4 = 0.43 = 43%
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Requirements of chemical reactions during volumetric analysis

a) Reaction must be simple & can be easily represented in the form of chemical equation HCl + NaOH → NaCl + H_2O Due to this quantitative relationship between reactant & product can be easily establish

b) The reaction must be sufficiently fast. High velocity/rate of reaction ensure errorless calculation of quantity of analyte./ The std. reagent & analyte instantly form the product.

c) The reaction must be stoichiometric: For non-stoichiometric reaction it is not easy to establish quantitative relationship bet. Reactant & product. HCl + NaOH → NaCl + H_2O is stoichiometric reaction
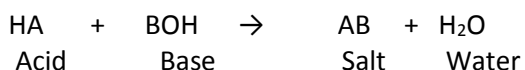$$1M \quad 1M \quad \quad 1M \quad 1M$$

d) Their must be a suitable physical change (Colour,turbidity) in solution as soon as reaction completed.

e) Suitable reagent (Indicator) must be available to bring required physical change on completion of reaction.

Types of volumetric analysis

- Classified On the basis of chemical reactions taking place during titrations
- Acid Base titration
- Oxidation Reduction Or Redox titration
- Iodometric titration
- Precipitation titration
- Complexometric titration

1. Acid Base titration (Neutralization titration)

- Principle: It involves reaction between acid / base, with Standard Base/ Acid result formation of salt & water. Here pH of mixture changes& approaches to 7 hence is called as *neutralization* titration or acid base titration.
  HA   +   BOH   →   AB   + H_2O
   Acid   Base   Salt   Water
  Objective: To determine exact volume of standard acid/base consume towards complete neutralization of analyte present in known volume of sample
  Acid Base reaction
  HCl + NaOH → NaCl + H2O
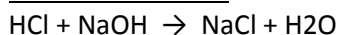
Basic requirements: Standard acid/base, Suitable acid-base indicator.

Types of Acid Base titration

- On the basis of Std. soln taken in burette during acid base titration we have two types
- 1. Acidimetry:
- The neutralization reaction between analytebase & standard acid is called as acidimetry titrations e.g. Alkalinity of water sample.
- 2. Alkalimetry:
- The neutralization reaction between analyte acid & standard base is called as alkalimetry titrations. E.g. Acid value of an oil.

Type of titration	Ideal pH range	pH at equivalence point	Choice of indicator
Strong Acid Vs Strong Base	4 to 10	7.0	M.O.(3.1-4.4) M.R.(4.2-6.3) P.P.(8.3-10)
Strong Acid Vs Weak Base	3 to 6.5	5.28	M.O.(3.1-4.4) M.R.(4.2-6.3)
Weak Acid Vs Strong Base	7.5 to 9.5	8.72	P.P.(8.3-10)
Weak Acid Vs Weak Base	6.5 to 7.5	7	i) No simple indicator ii) Mixed indicator

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Indicator for acid base titrations : Acid Base indicators are certain organic weak acid or bases undergoes visible colour change within specific pH range.

Selection of Indicators for Acid Base titrations
1. Types of A/B Titration, Acidimetry Alkalimetry 2. Ph at equivalence point 3. Titration between St.A Vs St.Base etc.

- For Acid base titration it is essential to know pH range at equivalence point (if not known it is not possible to choose appropriate indicator)which depends on types of acid base titration. i.e. StA VsStB (3-10), St A Vs Wk B (4-7,7-10), WkA VsWkB (6.5-7.5, not clearly distict)
- After knowing this, selected indicator undergoes visible colour change within required pH range is selected.
- E.g. For HCl Vs NaOH any acid base indicator works.
- StAVsStB tit are always preffered because pH range at eq.point is 3-10, in which all indicators works. While wkAVsWk B it is 6.5 to 7.5 it is difficult to get proper indicator hence generally avoided
- For st acid St b titration pH range at eq point is very broad (3-10) & all indicators works within this pH range.
- NaOH is 8tabilizes8 & work as secondary standard
- Alkalinity is due to OH-, CO3 -- & HCO3 – ions During estimation neutralization of OH - & CO3 __ represents 8tabil StB & Second is St A Vs Wk B . To detect two equivalence point two indicators are used.
- A/B indicators are organic Wk A/B because they 8tabilizes their resonating st before & after eq.point of titn
- StA WkB & vice versa uses limited indicators because pH range at eq point is very narrow (3 – 6.5) & very few indicator avilables.
- **Applications of Acid Base titrations** 1.Determination of strength of acid base samples. 2.Determination of Drug samples 3. Determination of caustic soda. 4. Determination of acidity & alkalinity of water samples.
- 5. Determination of Saponification value & Acid value of an oil sample. 6.Estimation of nitrogen by Kjeldahls's method.

Application of Acid Base titration Alkalinity estimation

- Definition: Alkalinity of water can be defined as tendency of water to neutralize acid.
- Causes: It is caused by increase in extent of OH^-, $CO3^{--}$ or HCO_3^- ions by hydrolysis, dissociation etc.
- Types: Based on this alkalinity of water is classified in three types.
- 1. Hydroxil or Hydrate alkalinity: due to OH^- denoted by A_H
- 2. Carbonate alkalinity: due to $CO3^{--}$ denoted by A_C
- 3. Bicarbonate alkalinity: due to HCO_3^- denoted by A_B
- The alkalinity of all three types will not exist at same time as existence of OH^- & HCO_3^- with each other is ruled out. The total alkalinity A is sum of Hydroxyl, carbonate & bicarbonate alkalinity.
- Disadvantages: Alkaline water is not suitable for domestic & industrial use. The important disadvantages of alkalinity are
- 1. Carbonate & bicarbonate alkalinity causes temporary hardness (Ca & Mg bicarbonate)
- 2. Alkaline water causes digestive disorders when used for drinking.
- 3. OH^- alkalinity causes caustic embrittlement of metallic components, spares, machines, equipments etc.

- 4. Alkalinity of water causes damage to constructions made on source of water e.g. Bridges
- 5. Alkaline water helps scale & sludge formation in boilers.
- 6. Continuous use of alkaline water for agriculture spoil the soil by change pH.
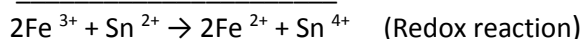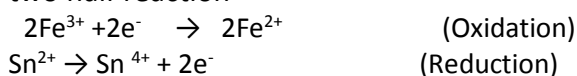
Result of titration to PP end point "p" & MO end point "m"	Hydroxide OH⁻	Carbonate CO₃⁻⁻	Bicarbonate HCO₃⁻
P= 0	Nil	Nil	M
P=M	M	Nil	Nil
P=1/2 M	Nil	2P	Nil
P> ½ M	2P-M	2(M-P)	Nil
P< ½ M	Nil	2P	(M-2P)

2.Oxidation Reduction Titration or Redox titration

- Principle: In involves reaction between analyte Oxidizing/ Reducing agents with standard reducing/ oxidising agents , result simultaneously exchange of electrons between them.
- Objective: To determine exact volume of standard reducing/ oxidising agent required to carry out reduction/ oxidation of anlyte present in known volume of sample using suitable/ self indicator.

Redox reaction

- When two suitable oxidizing & reducing agents are brought together, complete reaction is sum of two half reaction

    $2Fe^{3+} +2e^- \rightarrow 2Fe^{2+}$　　　　　(Oxidation)

    $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$　　　　　(Reduction)

    _____

    $2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$　　(Redox reaction)

   Requirements: Standard reducing/ oxidizing agent, Sitable Redox indicator.

    Redox Indicator: These are generally organic compound, either Oxidizing or Reducing form shows different color within definite potential range

- Interconversion of indicator can be represented by the following equation

    In (Oxidized form) $\leftrightarrow$ In (Reduced form)

- Diphenyl indicator is used for the titration of $FeSO_4$ Vs $K_2Cr_2O_7$ As long as Fe^{2+} ions (ferrous) are present in solution this indicator is colorless. After equivalence point all Fe^{2+} ions are converted into Fe^{3+} ions (ferric), $K_2Cr_2O_7$ oxidizes Diphenyl amine into Diphenyl benzidine which is violate in colour.

    Application of Redox titrations: 1Determination of COD in waste water $K_2Cr_2O_7$ as oxidizing agent. 2.Estimation of ferrous &ferric iron present in given solution. 3. Determination of chromium in chromate ore. 4.Estimation of calcium in lime stone by forming calcium oxalate by $KMnO_4$ 5.Estimation of manganese dioxide in pyrolusite.

Iodometric Titration:

It is integrated part of Redox titration.

The reduction of free iodine to iodide ion and oxidation of iodide ion to free iodine occurs in these titrations

$I_2 + 2e^- \rightarrow 2I^-$ (Reduction)

$2I^- \rightarrow I_2 + 2e^-$ (Oxidation)
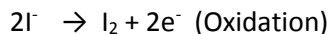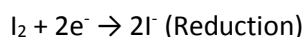
Principle: It involves reaction between anlyte reducing agent (loss of e) with standard solution of Iodine directly or Analyte oxidising agent react with iodide ions, convers iodide ions into Iodine, will be reacted with standard reducing agent using suitable indicator.

These titrations are divided into two types

Iodimetric titration & Iodometric titration

Iodimetric titration: Standard solution of Iodine react with anlyte reducing agent. It is one step reaction

$I_2 + 2e^- \rightarrow 2I^-$ This method is rarely used.

& Iodometric titration: In this titration Iodide ion react with analyte reducing agent and converted into Iodine molecule which is directly titrated with standard reducing agent using starch indicator.It is commonly used method. It two step reaction

Analyte Metal ion + $2I^-$ (from KI) → I_2 + $2e^-$

I_2 (Liberated Iodine) + $2 S_2O_3^{2-}$ (from Burette) → $2I^-$ + $S_4O_6^{2-}$
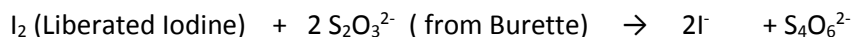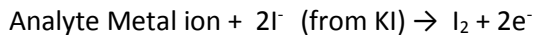
Indicator: Starch
In Iodometric titration freshly prepared starch solution is used. This indicator gives a deep blue colour with iodine. Color change of titration is blue to colorless

-

Comparision: Iodometry Iodimetry

• Iodometry	• Iodimetry
Analyte oxidizing agent added to excess iodine to produce iodine titrated with std. $Na_2S_2O_3$	Analyte reducing agent is directly titrated with std. iodine solution
Indirect method	Direct method
2redox rection occures	1 redox reaction occurs
Iodine gets oxidised first & then reduced by reducing agent	Iodine only gets reduced
More common to titration	less common to titration
E.g Cu, DO, IV, free chlorine etc	Sn2+ -Sn4+

Application of Iodometry: 1Determination of DO in water sample. 2.Determination of free chlorine in water sample. 3.Determination of iodine value of lubricating oil. 4.Determination of copper in a given sample of an alloy of copper. 5.Determination of available chlorine in the given sample of bleaching powder

Precipitation titration

- Principle: It involves reaction between analyte halides with standard precipitating agent result in the formation of a precipitate or slightly soluble salt of analyte sample
- Objective: To determining exact volume of standard precipitating agent required to form stable precipitate with component from sample, which is estimated in known volume using suitable indicator
- Generally precipitation titrations are used to estimate halides (Cl, Br, I) by using standard silver nitrate solution. This is also refereed as Argentimetry.
- Reaction:
- $NaCl + AgNO_3 → AgCl↓ + NaNO_3$
- White ppt
- $2AgNO_3 + K_2CrO_4 → Ag_2CrO_4 + 2KNO_3$
- Brick red
-

Requirements: Standard precipitating agent, Adsorption type of indicator.
Indicator: Chemical substance (Adsorbing)showing termination of reaction via visible colour change through adsorption of its own ppt on surface of parent ppt.
- Application: Estimations of halides in water sample (Cl, Br, I)
-

COMPLEXOMETRIC TITRATION

Complexometric titration is one in which a stoichiometric, undissociated, soluble complex is formed, during the addition of suitable complexing agent to the sample containing metal ions
- Principle: It involves reaction between analyte metal ions with standard complexing agent solution, resulting in the formation of stable complex of compound.
Objective: The objective is determining exact volume of standard complexing agent required to form stable complex with component from sample, which is estimated. The completion of complex formation is detected with suitable indicator
Requirements: Suitable complexing agent, Buffer solution & Suitable Indicator
Reaction:

EDTA Complex with bivalent charge
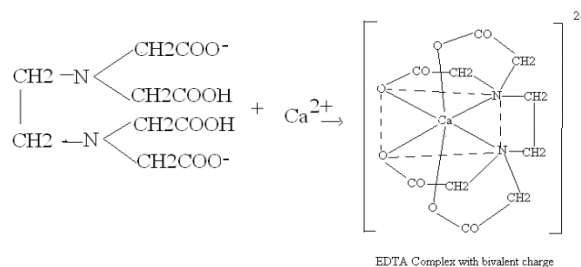
- <u>Complexing agent:</u> Definition: It is substance capable of forming complex with metal ion
- EDTA: (Ethylene Di amine Tetra Acetic Acid) The most commonly used complexing agent in complexometric titration.
- It is powerful chelating agent & forms high stable water soluble complex with almost all the metals.
- The metals are generally held in 1:1 ratio. This complex having five member rings

EDTA as versatile complexing agent

- Complexometry is one of the prime method in titrimetric analysis. It requies suitable complexing agent to prepare std. sol. EDTA is commonly used complexing agent in almost all complexometric titration because
- 1.It is readily available, available in sufficiently pure form and economical
- 2. Its disodium salt is Readily soluble in water.
- 3. It form complex with almost all metal ions.
- 4. It is sensitive to very low concentration of metal ions
- 5. It is selectivity towards specific metal ions under suitable pH.
- 6. Suitable masking agent must be available to avoid interferences of metal ion
- 7. They are suitable to carry out different types of complexometric titration like Direct,Back, replacement etc
- 8. They are sensitive to suitable indicator.

Role of pH/Selection of metal ions with pH i.e. complexing agents form stable complexes with metal ions at different pH levels

Metal ions	pH range
$Ca^{2+},Mg^{2+},Ba^{2+},Sr^{2+}$	9- 10
$Cu^{2+},Zn^{2+},Ni^{2+},Mn^{2+},Fe^{2+},\ Sn^{2+},Al^{3+}$	4-6
$Zr^{4+},Hf^{4+},Th^{4+},Bi^{3+},Fe^{3+}$	1-3

 <u>Indicator</u>: Coloured complexing agent forming coloured complex & showing termination of reaction via colour change through dissociation of complex
- e. g. Murexide, Eriochrome Black T, Pyrocatechol violet, Xylenol orange etc.

Types of EDTA titrations
1. Direct titration: It is titration of buffered sample solution with standard EDTA
2. Back titration: In this titration excess, known & standard EDTA is added in sample & unused EDTA is back titrated with standard metal ion solution.
3. Replacement titration: If any metal ion fail to form stable complex then it is replace by suitable ion & it is titrated with standard EDTA solution.
4. Alkalimetric titration: If no suitable indicator is available, then known excess of EDTA is added to sample & free H^+ ions formed are determined by titrating with standard base solution.

 <u>Applications:</u> 1.Determination of hardness of water sample. 2.Estimation of Zn in an alloy of brass. 3.Estimation of Ca in limestone. 4. Estimation of Ca & Mg in dolomite

 Appication: Estimation of hardness of water.

Advantages
1. It is generally cheap, requiring little in the way of equipment.
2. It does not require a high level of skill.
3. It can often be done rapidly.
4. Results are immediately available.

Disadvantages
1. It is a destructive method often using up relatively large quantities of the substance being analysed.
2. It requires reactions to occur in a liquid phase, often the chemistry of interest will make this inappropriate.
3. It can produce significant amounts of chemical waste which has to be disposed of.
4. It has limited accuracy.

Gravimetric Analysis

Introduction

The gravimetric analysis is type of quantitative analysis that deals with the determination of an element or ion or a compound obtained from a sample by weighing a suitable form of it accurately. It is one of the very important analytical technique that gives accurate and precise results.

Definition: This is quantitative analysis involves, determination of ion/ element/ component/ingredients by accurately weighing it into desirable compound having definite chemical composition.

1Analyte in solution form + Precipitating Reagent → Analyte converted into insoluble part called ppt, along with mother liquor → Filtration of ppt and washing of ppt with electrolyte having common ions

2→ Air drying → Drying in oven (100 to 200 ^{o}C) It is stable with weathering condition with fixed chemical composition→ Weighing & according to chemical formula Calculation of quantity of analyte   ---OR-----

2 → Air drying → Heating in oven (700 to 800 ^{o}C) till it converted into stable chemical composition → Weighing & according to chemical formula Calculation of quantity of analyte   -----OR----

2→ Filtered ppt dissolved into another solvent and reprecipitated by ppting agent.   And followed above 2 process so that final substance have definite chemical structure.

Some Important Terms

1. **Precipitate**: It is a insoluble solid separated from the solution as a result of chemical reaction.
2. **Precipitant**: It is a chemical reagent that forms precipitate on addition to solution.
3. **Precipitation**: It is a process of forming a precipitate due to chemical reaction.
4. **Peptisation**: It is a phenomenon in which the electrolyte concentration in the supernatant liquid may fall below the coagulation value and the precipitate may pass into colloidal solution again.
5. **Coagulation**: It is a process of forming gelatinous mass by complete or partial solidification of sol.
6. **Super saturated solution**: A solution containing greater concentration of solute is known a super saturated solution.
7. **Coagulation or flocculation value**: It is the minimum amount of electrolyte necessary to cause flocculation of the colloid.
8. **Sol**: It is a trerm used to distinguish the colloidal suspension from microscopic suspensions.
9. **Co- precipitation**: The simultaneous precipitation of more than one compound from a solution.
     The gravimetric analysis includes formation of the precipitate, (digestion of precipitate if necessary) filtration of precipitate. Washing of precipitate, drying and ignition of precipitate, accurate weighing of residue and determination of constituents using relations.
Types of Gravimetric Methods:

Precipitation gravimetry : In this method analyte ions/element/ component converted into suitable insoluble solid having fixed and stable chemical composition for accurate weighting. Thus from weight of compound of anlyte it estimated called precipitation gravimetry. e.g Determination of Cl$^-$ by precipitating it into insoluble AgCl.

Electro gravimetry : In this method analyte deposited on an electrode i.e cathode in the form of film by passing electric current and amount of element is direly determine by weighting it in the form of metal or some time weighing the liberated gases at respective electrode called electrogravimetry. E.g The deposition as PbO_2 at a Pt anode is one example of electrogravimetry. The reduction of Cu^{2+} to Cu at a Pt cathode is another example of electrogravimetry

Volatilization gravimetry : In this method thermal or chemical energy is used to remove a volatile species, so weight difference is obtained called volatilization gravimetry.

It is possible simply by measuring weight of residue left after removal of volatile matter OR allowing to absorb liberated volatile matter to some chemical substance, where increase in mass of absorbing substance recorded.

In determining the moisture content of bread, for example, we use thermal energy to vaporize the water in the sample. To determine the amount of carbon in an organic compound, we use the chemical energy of combustion to convert it to CO_2

Particulate gravimetry: In particulate gravimetry we determine the analyte by separating it from the sample's matrix using a filtration or an extraction. The determination of total suspended solids is one example of particulate gravimetry.

Thermogravimetry: In this method analyte is subjected to thermal treatment and change in weight of substance is recorded as function of temperature using thermogravimeter called thermo gravimetric analysis. Determination of moisture content, volatile matter content, thermal decomposition of matter, rusting of material where mass of sample increase or decrease measured by thermo balance.

Organic precipitation gravimetry: This method is similar to precipitation gravimetry but precipitating agent used is organic substance e.g. Ni + DMG → [Ni-DMG]

Characteristics of precipitate

The accuracy and precision of gravimetric analysis mostly depended on the nature of precipitate formed. **So the precipitate should possess following characteristic properties**-

1. The precipitate should have **low solubility** otherwise practically complete precipitation is not possible.
2. The form of precipitate should be such as to **allow rapid filtration and washing**. Since it saves time during analysis and give errorless quantity.
3. The **composition** of precipitate should be **strictly according to its chemical formula**. It should not contain water of crystallization. Otherwise error occurs during analysis.
4. The precipitate should have adequate **chemical stability** and it should not absorb moisture or gases from atmosphere. i.e inert to the weathering condition

Precipitation

A) Requirement for good precipitation / General rules for good result of precipitation

No universal rules can be given which are applicable to all cases of precipitation. However, there are **some general rules for good result of precipitation**.

1. Precipitation should **be carried out in dilute solution** to **avoid the chance for co precipitation** (The simultaneous precipitation of more than one compound from a solution). Of course the solubility of the precipitate, the time required for filtration should not be ignored.
2. A suitable reagent should be **mixed slowly and with constant stirring**. This assists the growth of crystals and keeps a low value of super saturation.
3. Precipitation is generally carried out in **hot solutions**, which decreases chance of super saturation as solubility increases with rise in temperature and hot solution favours coagulation and **rapid growth**.
4. The precipitate should be **digested for prolonged period to avoid co-precipitation**.
5. The precipitate should be **washed** thoroughly with appropriate dilute solution of an **electrolyte containing common ions, instead of pure water which leads to cause peptisation**.
6. Many time precipitate is dissolved in suitable solvent and then reprecipitated to eliminate contamination.

   The solubility of precipitate, excess of precipitant, pH of the solution, temperature and the nature of solvent, affect the yield of precipitate in gravimetric analysis.

B) Process of precipitate

The process of precipitation includes three stage viz, (1) Nucleation (2) Crystal growth and (3) Ageing i.e. recrystallization.

1. **Nucleation**: The <u>nuclei provide centres</u> at which subsequent growth takes place.
   Nucleation possible by two ways
   i) <u>In dilute solution</u> very fine suspended <u>foreign matter</u> in the solution (i.e dust) or impurities adhering to the walls of the glass vessel.
   Such nucleation processes are <u>called as heterogeneous</u>,
   ii) In super <u>saturated solution   ions</u>/ cluster/crystals of same substance provide centre.
   This nucleation process is said to be <u>homogeneous</u>,

   Hence it is possible to say that, nuclei were forming spontaneously in the solution in which the precipitate was actually growing on invisible, additional nuclei that were already present.

2. **Crystal growth** : Once crystal nuclei are formed, crystal growth starts by the transport of corresponding ions from the solution to the growth crystal. Crystal growth depends on concentration of solution, temperature of solution, stirring of solution.

3. **Ageing/ Digetion** of precipitate : After complete precipitation usually it is allowed to digest

   before filtering. The particles become larger, more perfect and easier to filter as a result of digestion. This results by the disappearance of smallest particles.

   Since it is spontaneous process, result in decrease in free energy at constant temperature and therefore all surfaces tend to become as small as possible. The solid can reduce it's surface area by aggregating to form a larger particles since the small particles have more surface area per unit mass than larger one. But solid is rigid, hence martial goes into solution from the small particles and redeposit on large particles.

   During the process of digestion following changes take place. **Effects of digestion**

   i)   Originally irregular particles are converted in to more compact from
   ii)   Decrease in surface area result to reduce the surface adsorption.
   iii)   Decrease in co precipitation.

iv)   Internal perfections may even occur simply by diffusion of atoms with the solid.

v)   The colloidal particle may become cemented together by depositing solid between them.

But the precipitate of AgC1 and hydrous Fe_2O_3 remain colloidal even after long digestion. This may be because of too small value of surface energy.

In some cases the electric charge on the particle of precipitate may hinder Ostwald ripening because of high electro kinetic potential of the particles.

If the impurities are less soluble than main precipitate, than digestion may increases amount of co-precipitate? Under such circumstance responsible ions should be removed from the solution or should be masked before precipitation.

Physical Nature of Precipitate

The Physical forms of precipitates can be classified as

(i) Crystalline ppt : The crystalline precipitates size 0.1 to 1 micron in diameter

(ii) Curdy ppt : The curdy have intermediate size 0.02 to 0.1 micron

(iii) Gelatinous ppt : Gelatinous precipitates have smaller particle size less than 0.02 micron

Gelatinous ppt is not possible to filter the curdy and gelatinous precipitates as they have very fine particles which easily pass through filtering media . These precipitates are held together by weak cohesive forces and get easily dispersed or peptized which can be prevented by washing with an electrolyte instead of pure water as they carry indefinite amount of water

The physical form of these precipitates are inter-convertible. For example curdy precipitate of AgCl is converted in crystalline from when it's solution in aqueous ammonia is slowly evaporated. Similarly gelatinous precipitate of $Al(OH)_3$ is converted into crystalline form by slow evaporation of it s solution with concentrated aqueous ammonia thus physical nature of precipitate largely depends upon the size shape and electric charge on the particles of precipitate.

Purity of Precipitate

The greatest source of error in the gravimetric analysis is the impurity of the precipitate which results due to co-precipitation & post precipitation.

Co-precipitation: The contamination of the precipitation by substances which are normally soluble in the mother liquor during its formation is known as co-precipitation.

For example, the precipitation of nickel dimethylglyoxime requires a slightly basic pH. Under these conditions, any Fe3+ in the sample precipitates as Fe(OH)3. In addition, because most precipitants are rarely selective toward a single analyte, there is always a risk that the precipitant will react with both the analyte and an interferent.

It may result by two ways a) by formation of solid solution b) by surface adsorption.

a) **By formation of Solid Solution:** The solid solution formation means the formation of mixed crystal which result in actual entering the impurities in the crystal lattice of the precipitate.
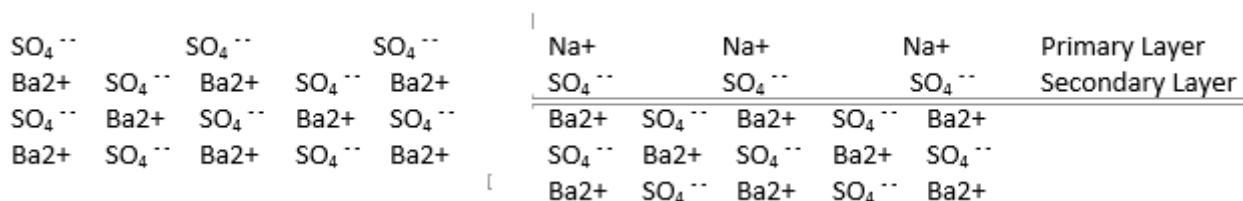
Conditions required forming solid solution

i) The activities of the dissolved substance & precipitate should be equal.

ii) Both the solid should be isomorphism (i.e. they should be crystalline the same form.)

iii) The difference between ionic radii of like signs should not be more than 10 %

Since condition for solid solution formation is being very strict, this type of co-precipitation is rarely observed. However it can be avoided simply by digestion of precipitate.

b) **By surface adsorption.** : It results by the process of occlusion(prevention). The amount of co-precipitation results by surface adsorption depends upon the physical nature of the precipitate.

Crystalline Precipitate: Freshly formed precipitate has large surface area either because if its very small particle size or imperfectness. The electric charge is the origin of the surface adsorption.

e.g. The crystal lattice of B_aSO_4 contains alternative arrangement of Ba^{+2} & SO_4^{-2} ions. When it is placed in Na_2SO_4 solution its crystal lattice grows due to excess of SO_4^{-2} ions by adsorbing SO_4^{-2} ions on the surface of it. This gives negative charge to the $BaSO_4$ crystal. This layer of adsorbed SO_4^{-2} ions called primary layer, which attracts the Na^+ ions from the solution, as a result SO_4^{-2} crystal lattice gate adsorbed with Na_2SO_4 layer as shown in the figures below

$SO_4^{..}$		$SO_4^{..}$		$SO_4^{..}$		$Na+$		$Na+$		$Na+$		Primary Layer
$Ba2+$	$SO_4^{..}$	$Ba2+$	$SO_4^{..}$	$Ba2+$		$SO_4^{..}$		$SO_4^{..}$		$SO_4^{..}$		Secondary Layer
$SO_4^{..}$	$Ba2+$	$SO_4^{..}$	$Ba2+$	$SO_4^{..}$		$Ba2+$	$SO_4^{..}$	$Ba2+$	$SO_4^{..}$	$Ba2+$		
$Ba2+$	$SO_4^{..}$	$Ba2+$	$SO_4^{..}$	$Ba2+$		$SO_4^{..}$	$Ba2+$	$SO_4^{..}$	$Ba2+$	$SO_4^{..}$		
						$Ba2+$	$SO_4^{..}$	$Ba2+$	$SO_4^{..}$	$Ba2+$		

This type of co-precipitation can be removed by the digestion.

Curdy Precipitate: The surface adsorption results through same mechanism as in case of crystalline precipitate. The difference between curdy & beyond colloidal size. They do not therefore enclose impurities by growing around them & can be removed by washing with dilute solution of suitable electrolyte.

Gelatinous Precipitate: Being smaller particle size it provides large surface area that results in strong surface adsorption which can not be removed either by digestion or washing the precipitate. The co precipitation in this case can be prevented by caring out the precipitation at suitable pH.

Post Precipitation: The appreciable errors may be introduced by post precipitation. This is the precipitation which occurs on the surface of the first precipitate after its formation. It occurs with sparingly soluble substances which form supersaturated solution; they usually have an ion in common with the primary precipitate. Thus in the precipitation of calcium as oxalate in the presence of magnesium, magnesium oxalate separate out gradually on the surface of calcium oxalate. The longer the precipitate is allowed to stand in contact with the solution greater is the error due to this cause. Similar effect is observed in the precipitation of copper or mercury (II) sulphide in 0.3M HCI, in the presence of zinc ions, zinc sulphide is slowly post precipitated. This error may be avoided by i) filtering the precipitate immediately after precipitation, ii) caring out precipitation at critical pH iii) protecting the ions responsible for this error by masking.

Difference between post precipitation & co-precipitation

Post precipitation is distinguished from co-precipitation in the following ways-

i) The magnitude of contamination by post precipitation may be greater than in co-precipitation.

ii) Rise in temperature increases rate of contamination by post precipitation.

iii) The contamination increases with time as the main precipitate is left in contact with the mother liquor in post precipitation, while it decreases in co-precipitation.

Numerical:

1. A 0.7336-g sample of an alloy containing copper and zinc is dissolved in 8 M HCl and diluted to 100 mL in a volumetric flask. In one analysis, the zinc in a 25.00-mL portion of the solution is precipitated as ZnNH4PO4, and subsequently isolated as Zn2P2O7, yielding 0.1163 g. The copper in a separate 25.00-mL portion of the solution is treated to precipitate CuSCN, yielding 0.2931 g. Calculate the %w/w Zn and the %w/w Cu in the sample.

A conservation of mass requires that all the zinc in the alloy is found in the final product, Zn2P2O7. We know that there are 2 moles of Zn per mole of Zn2P2O7; thus

$$0.1163 \text{ g } Zn_2P_2O_7 \times \frac{2 \text{ mol } Zn}{304.72 \text{ g } Zn_2P_2O_7} \times$$

$$\frac{65.39 \text{ g } Zn}{\text{mol } Zn} = 4.991 \times 10^{-2} \text{ g } Zn$$

This is the mass of Zn in 25% of the sample (a 25.00 mL portion of the 100.0 mL total volume). The %w/w Zn, therefore, is

$$\frac{4.991 \times 10^{-2} \text{ g } Zn \times 4}{0.7336 \text{ g sample}} \times 100 = 27.22\% \text{ w/w } Zn$$

For copper, we find that

$$0.1163 \text{ g } CuSCN \times \frac{1 \text{ mol } Cu}{121.64 \text{ g } CuSCN} \times$$

$$\frac{63.55 \text{ g } Cu}{\text{mol } Cu} = 0.1249 \text{ g } Cu$$

$$\frac{0.1249 \text{ g } Cu \times 4}{0.7336 \text{ g sample}} \times 100 = 67.88\% \text{ w/w } Cu$$

2. a 2.00 gm sample of limestone was dissolved in hydrochloric acid and all the calcium present in the sample was converted to Ca2+ ion. Excess ammonium oxalate solution, (NH4)2C2O4(aq), was added to the solution to precipitate the calcium ion as calcium oxalate, CaC2O4(s). The precipitate was filtered, dried and weighted to a constant mass of 2.43gm. Determine the % by mass of calcium in the lime sample.(MW CaC2O4= 128.097, CaCO3=100)
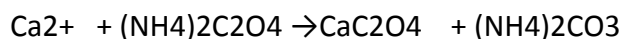
Ca2+ + (NH4)2C2O4 →CaC2O4 + (NH4)2CO3
Wt of CaC2O4 ppted = 2.43gm
Hence number of moles = 2.43/128.097 = 0.0189
Hence wt of CaCO3 = 0.0189 X 100 = 1.89gm
2.0 gm of sample cotain 1.89gm Ca Hence Purity = 1.89 X100/2 = 94.8499%
3. A 3.00 gm sample of an alloy (conaining only Pb and Sn) was dissolved in HNO3. H2SO4 was added to this solution, which precipitated 1.69gm of PbSO4. Assumeing that all of the Lead was precipted, what is the percentage of Sn in the sample?
3 gm of alloy (Pb & Sn) contain 1.69 gm of PbSO4 (MW 303.26)
Amount of Pb (MW 207.2) in PbSO4 = 207.2 X 1.69/303.26 = 1.1546gm
Hence Wt of Sn = 3.00 – 1.1546 = 1.8453

Hence % of Sn = 1.8453 X100 / 3 = 61.51%

4. An empty crucible has a mass of 12.770 gm. The crucible and hydrate have a mass of 13.26gm. after heating, the crucible and anhydrous salt have a mass of 13.010 gm. What is formula of this hydrate of MgSO4. ?H2O? (MW MgSO4 = 120.366)

Crusible weight = 12.770gm

Crusible + Hydrated MgSO4 wt = 13.26gm

Crusible + unhydrated MgSO4 wt = 13.01gm

Wt of Hydrated MgSO4 = 0.49gm

Wt of Unhydrated MgSO4 = 0.24gm

Wt of Moisture = 0.25gm

For 0.24 gm MgSO4 , wt of moisted MgSO4   is 0.49gm

Then what is wt of 120.366 gm of MgSO4? = 120.366 X 0.49 / 0.24 = 245.7472 gm

Hence Amount of Moisture = 245.7472 gm - 120.366 gm = 125. 3812gm

18.01 gm H2O = 1 Mole

Hence 125. 3812gm = 125. 3812gm /18.01 = 6.96 Appox 7.00

Hence formula for MgSO4. ?H2O = MgSO4. 7H2O

   Advantages of Gravimetric:

 1.It is accurate and precise when using modern analytical balance.

2.   Possible sources of error are readily checked since filtrates can be tested for completeness of precipitation and precipitates may be examined for the presence of impurities.

3. It is an absolute method; it involves direct measurement without any form of calibration being required.

4.   Determination can be carried out with relatively inexpensive apparatus; the most expensive items are a muffle furnace and sometimes platinum crucibles.

5. Gravimetric analysis was used to determine the atomic masses of many elements to six figure accuracy.

6.   Gravimetry provides very little room for instrumental error and does not require a series of standards for calculation of an unknown.

Disadvantages of gravimetry:

1. The chief disadvantage is that it requires meticulous time consuming.

2.   The chemist often prefers modern instrumental methods when they can be used.

3.   Gravimetric analysis usually only provides for the analysis of a single element, or a limited group of elements, at a time.

4.   Methods are often convoluted and a slight mis-step in a procedure can often mean disaster for the analysis (colloid formation in precipitation gravimetry, for example).

5.   Gravimetric analysis is based on the measurement of mass**.**

GRAVIMETRIC ANALYSIS
V E R S U S
VOLUMETRIC ANALYSIS

GRAVIMETRIC ANALYSIS	VOLUMETRIC ANALYSIS
Gravimetric analysis is a process of measuring the amount of an analyte by its mass	Volumetric analysis is a process used to determine the amount of a desired constituent by its volume
Mass of the analyte is determined	Volume of the analyte is determined
Involves the formation of a solid mass known as a precipitate, which can be separated from the sample solution	Done via a titration, in which the volume of analyte is determined by adding portions of a reagent that can react with the analyte
Generally gives the final result in grams	Gives the final result in milliliters

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