

## UNIT-I

# INTRODUCTION TO ANALYTICAL CHEMISTRY AND STATISTICAL TREATMENT OF ANALYTICAL DATA

### 1.0. Introduction:

Analytical Chemistry is a branch of chemistry which deals with the study of theory and practice of methods used to determine the composition of matter.

#### Application of Analytical Chemistry:

Analytical chemistry is applicable to each and every branch/field. If one tries to prepare the list of applications, the list will be unending. All industries, irrespective of what they produce, all of these depend upon the applications of analytical methods. The application of analytical chemistry is as follows;

- a) Research and Development :
- b) Quality control unit :
- c) Organic Industry :
- d) Pharmaceutical industry:
- e) Metallurgical Industry :
- f) Electronic Industry:
- g) Environmental pollution:
- h) To check the purity of water:
- i) Industrial Effluent Analysis:
- j) To Control the Air Pollution:

### 1.1 Role of Analytical Chemistry :

#### 1.1.1 Language of Analytical Chemistry : Terms Involved in Analytical Chemistry

##### Definition of terms:

i) **Precision:**

*It is the agreement between individual observations of the same set.*

ii) **Accuracy:**

*It is defined as the closeness of the observed value with the true value.*

iii) **Limit of detection (LOD):**

Minimum amount of concentration of a component that can be detected with a given degree of confidence

iv) **Limit of Quantification (LOQ):**

Minimum amount of concentration of a component that can be estimated with a given degree of confidence is termed as LOQ.

v) **Limit of Linearity (LOL) :**

It is defined as maximum concentration range up to which instrument produces linear response.

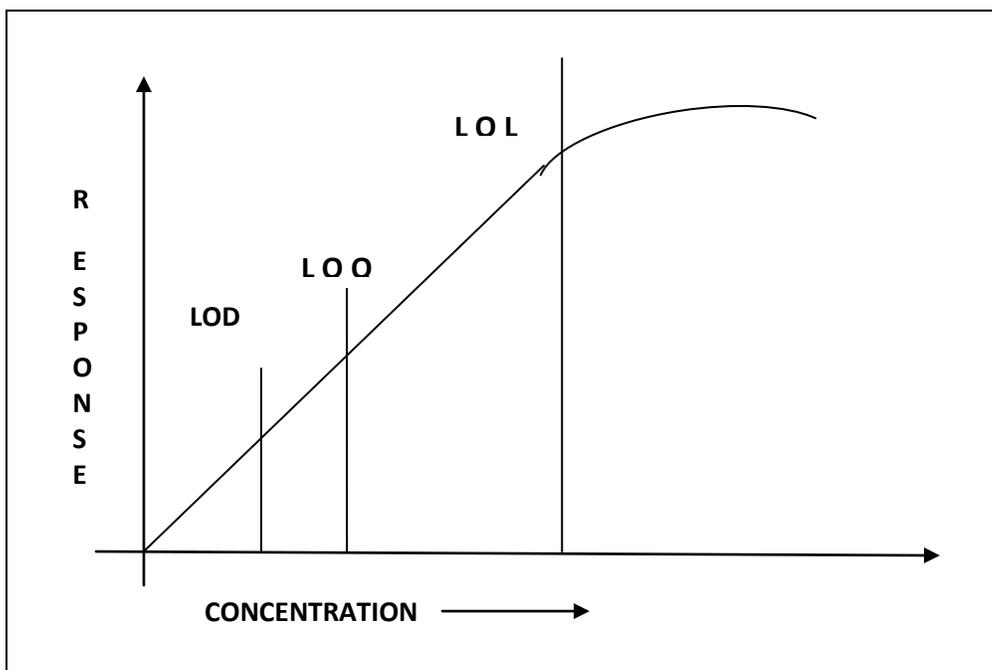
vi) **Sensitivity:** *It is a measure of ability of method to discriminate between two small concentration differences in the analyte*

*Sensitivity is measured in terms of slope of the calibration curve. If the slope is greater sensitivity of the method is high and vice-versa.*

vii) **Selectivity:** *It is defined as degree to which the method is free from interferences from other components present in the matrix.*

viii) **Dynamic range:**

It is the concentration range from limit of Quantification (LOQ) to Limit of Linearity (LOL).



- ix) **Reproducibility** : It represents the precision between laboratories.
- x) **Robustness** : A method that can be applied to analytes in a wide variety of matrices is considered robust.
- xi) **Ruggedness** : A method that is insensitive to changes in experimental conditions is considered rugged.

### 1.1.2 Purpose of Chemical Analysis:

- To characterize raw materials,
- Control the environment
- Asses the chemical safety of the product

It provides the information of a sample .

Analysis in general classified into two types;

- i. Nature of Information required
  - ii. Size of sample material
- i) **Based on information required the analysis is done in the following ways ;**
- a) **Proximate Analysis** : Amount of each element is determined with no concern of sample. Ex. Proximate analysis of Coal which includes determination of Moisture, Volatile compounds, Ash content, fixed carbon
  - b) **Partial Analysis** :It involves determination of selected constituent in the sample
  - c) **Trace analysis** : It involves determination of specified components in the sample in a very minute quantity.
  - d) **Complete analysis** : It involves determination of proportion of each components in the sample .
- ii) **Size of sample material: Based on size of sample used types of analysis are classified as follows;**
- a) **Macro analysis**: Size of the sample ranges from more than 100 mg or more than 100uL
  - b) **Semi micro analysis**: Size of the sample ranges in between 10 mg- 100 mg or volume between 50-100 uL.
  - c) **Micro analysis**: Size of the sample ranges in between 1 mg- 10 mg or volume less than 50 uL.

### 1.1.3 Analytical Methods:

The analytical methods can be divided into two major groups. They are;

- A) Classical methods (Chemical methods)

## B) Non-Classical methods (Physical Methods)

The chemical methods are also called as classical methods whereas the physical methods are known as instrumental methods of analysis.

**A) Classical methods: Classical methods** are the techniques which are the fundamentals of laboratory practices. These are the traditional method of chemical analysis which is still being used by scientists even up to this date.

These methods are also called as chemical methods, these methods based on performance of chemical reaction .

### **Chemical methods:**

The methods which are based on performance of chemical reaction are called as Chemical methods.

**Qualitative Analysis:** Analysis which deals with the identification can be called as qualitative analysis.

**Quantitative Analysis:** Analysis which deals with the determination of quantity of substance can be called as quantitative analysis.

Advantages of Classical methods:

- i) Simple procedures
- ii) Cheaper equipment
- iii) No specialized training required

### **1.1.4 Classification of Chemical Methods of Analysis**

Chemical Methods of Analysis are of two types;

- i. Gravimetry or Gravimetric analysis
- ii. Volumetry or Volumetric analysis

#### **i) Gravimetry**

Gravimetric analysis means analysis by weight and deals with all determinations wherein the final results are obtained by means of the analytical balance.

Gravimetry is an accurate macro- quantitative analysis procedure which mainly depends upon precipitation reaction. The precipitate obtained is digested, washed, separated by filtration, dried and weighed in the suitable form. The amount of the desired constituent (*analyte*) is then determined by simple calculation.

*Ex. i) Estimated barium as barium sulphate following gravimetric analysis.*

*ii) Estimation of Nickel as Ni-DMG.*

**Disadvantage:**

- i) Gravimetric method involves number of steps
- ii) The reaction does not undergo 100 % completion.
- iii) Mistake in one step creates error in accurate determination.
- iv) Time require for determination is very long.

**ii) Volumetry**

The amount of the analyte can also be found in another way by measurement of the volume. The method based on accurate measurement of volume of a reagent solution of accurately known concentration, taken for a reaction is known as *volumetric analysis*. The measurement of volume makes considerable saving of time. The greater speed of volumetric analysis is an important advantage of this method over gravimetry.

The volumetric analysis is characterized by a titration, hence the method is also known as *titrimetry*. In this method a known volume of the reactant substance is taken in a beaker and the titrant is added from a burette to it till the reactant completely reacts with the titrant. We call it as the equivalence point which is indicated by an indicator. The volume of the titrant required to reach the equivalence point is noted on the burette and the calculations are made to get the amount of the constituent of the reactant.

**Advantage:**

- v) The volumetric method is much simpler than the gravimetric method.
- vi) The reaction undergoes almost 100 % completion.
- vii) The method gives accurate determination than gravimetry.
- viii) Time require for determination is very short.

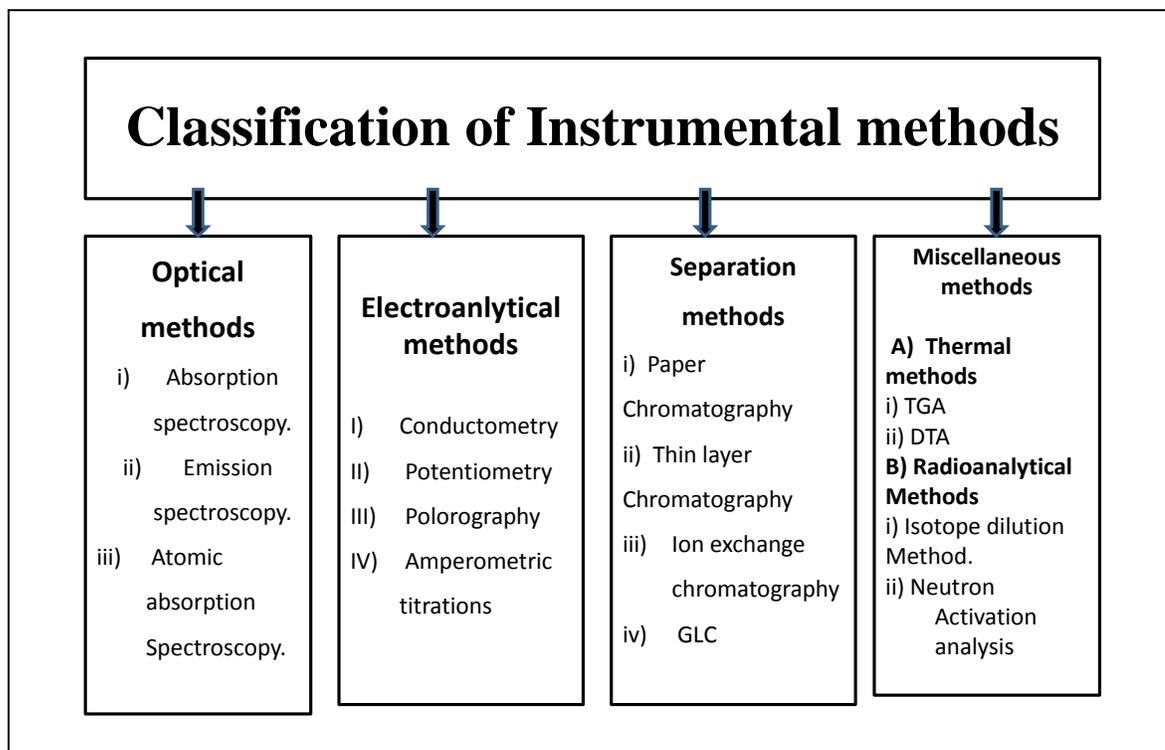
Depending upon nature of reaction involved in titrimetric analysis, It is classified into following categories.

- i) Acid base titration:** A titration in which neutralization reaction takes place  
Ex. Titration of HCl against NaOH
- ii) Precipitation titration:** A titration in which precipitation reaction takes place  
Ex. Titration of NaCl against AgNO<sub>3</sub>
- iii) Complexometric titration:** A titration in which Complexation reaction takes place  
Ex. Titration of Zinc sulphate against disodium salt of EDTA
- iv) Redox titration:** A titration in which redox reaction takes place  
Ex. Titration of Ferrous sulphate against Potassium dichromate

## ***B) Physical or Instrumental Methods:***

The methods which are based on measurement of physical property are called as physical methods. To measure physical property Instruments are used so physical methods are also called as Instrumental Methods.

### ***Classification of Instrumental Methods:***



### ***1) Optical Methods of Analysis:***

The method in which optical property such as optical density or absorbance, emission intensity, optical activity is measured as function of concentration is called as Optical Methods of Analysis.

#### **Types of Optical Methods of Analysis:**

All spectroscopic methods are based on the interaction of electromagnetic radiation with the quantized energy states of the matter. Here we study the measurement of a quantity based on emission, absorption, scattering or change in some property of electromagnetic radiation.

**i) Ultraviolet and Visible Absorption Spectroscopy:** In this methods absorbance of solution is measured by passing monochromatic light either in Ultraviolet or visible region.

The instrument used to measure absorbance /optical density in visible region called as Colorimeter or Photometer.

The instrument used to measure absorbance optical density in visible and ultra violet region called as Spectrophotometer.

Absorbance is directly proportional to concentration.

By using this technique qualitative and quantitative analysis can be carried out.

### **ii) Emission Spectroscopy:**

In this technique Emission Intensity is measured using the instrument called as Flame photometer.

Emission intensity is directly proportional to concentration.

By using this technique qualitative and quantitative analysis can be carried out.

### **iii) Atomic Absorption Spectroscopy:**

In this technique absorbance is measured using the instrument called as Atomic absorption Spectrophotometer.

Absorbance is directly proportional to concentration.

***Other optical methods are as follows;***

iii) Infrared Absorption Spectroscopy

v) Fluorophotometry

vi) Turbidimetry and Nephelometry

vii) Raman Spectroscopy

## **2) Classification of Electrical or Electroanalytical Methods of Analysis**

An electrical method of analysis also known as electroanalytical method can be defined as one, in which an electrochemical property of a solution is measured.

A classification of Electroanalytical methods can be made by measuring different electrical quantities, such as, potential, current, quantity of current, and resistance. These methods have different names on the basis of the measurement of these quantities and are stated below.

i) Potentiometry

ii) Amperometry

iii) Conductometry

iv) Polarography

### **i) Potentiometry:**

Analytical methods based on the measurement of potential difference (Cell potential) across an electrochemical cell to carry out analysis are called as Potentiometry.

In this technique cell potential is measured using the instrument called as Potentiometer.

Potentiometry can be used to carry out titration to find out equivalence point of a titration known as *potentiometric titration*. In potentiometric titrations we discuss redox titration curves based on half-cell potentials.

The instruments to measure Cell potential called as potentiometer.

### ***pH-metry***

The instruments used to measure pH of solution called as pH meter. To measure pH of solution a combine electrode (**Glass + Calomel**) is placed in the solution and electrodes are connected to pH meter.

pH of a solution is inversely proportional to Hydrogen ion concentration.

By using pH metry titration can be carried out called as pH metric titration.

### **ii) Amperometry**

Amperometry denotes the methods involving current measurements.

Amperometric methods are generally applied to the detection of equivalence point of titration and method is known as amperometric titration Here the current at a fixed potential is measured as a function of titrant volume. On plotting the data two straight lines with different slopes are obtained on both the sides of equivalence point.

### **iii) Conductometry:**

The measurement of conductance (the reciprocal of the resistance) can be useful in chemical analysis. Methods based on electrical conductance measurements are term as Conductometry. Conductometry is performed in two different ways:

In one an analysis can be computed directly from conductance measurements and in other Conductometry is applied to the determination of the equivalence point of titrations called as Conductometric titrations.

The instrument to measure Electrical conductivity is called as Conductivity meter.

Electrical conductivity is directly proportional to concentration of ionic species present in solution.

iii) **Polorography: It is** voltammetry technique in which electrolysis of an electrolyte is carried out using special type of micro electrode, called as the *dropping mercury electrode* as an indicator electrode .

The current versus applied potential curves are plotted. These curves are known as the current

Voltage curves or current-potential curves or I-E curves. From diffusion current Quantitative analysis can be performed.

### 3) Classification of Nuclear Methods/Radio analytical Methods:

**Radio analytical Methods** can provide analytical information based on nuclear properties. Each of these properties or combinations of them can be studied suitably by analytical chemistry.

#### v) Isotopic Dilution Methods:

In an isotopic dilution method a known amount of the same substance containing an active isotope is added to the unknown and thoroughly mixed with it. A sample of the pure substance is then isolated from the mixture and its activity is measured. The quantity of the substance in original material is then determined by simple calculation.

Ex. Na<sup>24</sup> Isotope is injected in human body to know Volume of blood present in human body.

#### ii) Neutron Activation Analysis:

In **Neutron Activation Analysis** thermal neutrons from a nuclear reactor are the most commonly used particles for activation.

In neutron activation analysis non radioactive substance is converted into radioactive substance by bombarding neutron on it. Radioactivity induced is measured in terms of gamma(γ) radiation.

*Some of other Radioanalytical techniques are as follows.*

iii) Mossbauer Spectroscopy

iv) Nuclear Magnetic Resonance Spectroscopy

v) Mass Spectrometry

### 4) Classification of Separation Methods

Sample contains different elements/ constituents, It is, therefore, frequently necessary to perform quantitative separations. The main with the objective is to remove the interfering substances. Therefore separation is a essential procedure for such determinations.

Though separation is not a purely analytical technique but it is commonly required prior to many analyses.

#### i) Classical methods:

In classical methods the constituents are separated either by distillation, filtration, centrifugation, and then individual determination is carried out.

#### ii) Modern methods

##### a) Chromatography:

*Chromatography* is a multistage separation process in which the sample is applied on a stationary phase over which a mobile phase is passed. Various solutes present in the sample are separated on the basis of differential migration.

**b) Solvent extraction:**

In *solvent extraction*, a desired solute can be isolated / extracted by distributing it between two immiscible liquids. It exploits the differential solubility of a given solute in two immiscible solvents to separate it from the given mixture.

**c) Ion-Exchange:**

*Ion exchange* is a stoichiometric process in which a solid (insoluble) material reversible exchange of ions having like sign takes place.

The solid materials having cations as exchangeable ions are known as *cation exchangers* and having anions as exchangeable ions are known as *anion exchangers*.

**d) Electrophoresis:**

The movement of charged particles under the influence of an electric field, is known as *electrophoresis*. If the components of a mixture have different velocities under the influence of the electric field, it is possible to separate them.

This method has been used with remarkable success for the separation and characterization of polysaccharides, nucleic acids, hemoglobin's

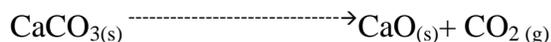
**5) Classification of Thermal Methods of Analysis**

In thermal methods of Analysis some property of the system is measured as a function of temperature. Commonly used methods are:

**i) Thermogravimetric Analysis (TGA):**

*Thermogravimetric analysis* (TGA) involves the measurement of mass of a sample as function of time or temperature. In this method when sample undergoes physical and chemical change.

Ex. Decomposition of Calcium carbonate



**ii) Differential Thermal Analysis (DTA)**

In *differential thermal analysis* (DTA) the difference in temperature between sample and reference is measured as a function of temperature.

From the plot of DT versus T. the transition temperature and the nature of the change (exothermic or endothermic) can be determined.

## 1.2 Sampling:

### Significance of sampling in Analytical Chemistry:

**1.2.1 Purpose of sampling :** The purpose of sampling can be more than one.

i) **Judging acceptability:** By taking out a sample and doing analysis. The data is compared with purchase or sales specification. From the analytical data one will decide whether to buy bulk or not .

For this purpose sample should represent the whole quantity under consideration  
Frequently more than one sample is to be taken and analysis must be performed on each step of the sample drawn.

ii) **Detecting Contamination:** The second Objective or purpose of sampling is to ensure that material is free from contamination.

By taking out a sample and doing analysis, one will come to know about the level of impurities.

ii) **Identification of Material:** Third purpose of sampling is to identify the material. A carefully drawn the sample can accurately give information of the material.

**(Question: Describe the purpose or importance of sampling)**

#### 1.2.2 What are difficulties encountered in sampling:

1) *Lack of prior information:*

2) *Physical Nature: Ex. In pile of coal ,the interior portion is not easily available Or sampling of rock material is difficult.*

3) *Excessive cost: Time, labour, and money.*

*Ex.if sampling units are too large, sampling cost will go up.*

#### 1.2.3 Terms involved in the sampling:

**Question: Define the following terms( 2 marks each Defination)**

i) **The Population or Universe:** The bulk material from which sample is to be drawn is termed as Population or Universe.

ii) **Sample:** A small portion of the universe drawn for the purpose of analysis and which posses all essential characteristics of the universe is called as sample.

iii) **Sampling Techniques or Procedures:** The series of steps that is to be carried out to obtain a sample Sampling Technique or sampling procedure.

iv) **Sampling Unit:** The minimum size package in the consignment which sample may represent is known as sampling unit.

- v) *Increment*: A stated amount of the material that is withdrawn from the sampling unit is defined as Increment.
- vi) *Gross Sample*: The total sample obtained by mixing or blending all increments is known as gross sample.
- vii) *Sub sample*: A smaller size sample produced by subdivision of the gross sample and which posses all essential characteristics of the gross sample is known as sub-sample.
- viii) *Analysis Sample*: An accurately weighed amount of sub sample taken actually for analysis is known as analysis sample.

#### 1.2.4. Types of Sampling:

**Question:** Describe / explain the types of sampling?

i) **Random sampling:** Random sampling involves the selection of material without any bias or prejudice. In this method every part of bulk material has an equal chance of being picked up as a sample.

This technique of sampling requires a minimum knowledge of the universe under consideration. If the material is homogenous it is easy to sampling. If the material is heterogeneous the bulk is divided into relatively homogenous different groups. Then sample is withdrawn, at any time ,from any part of group.

#### Advantages of random sampling

- i) *It is unbiased*
- ii) *Every part of bulk has equal chance of being selected as sample*

ii) **Non random sampling:** Sampling is carried out in more scientific way than random sampling. In this sampling better sample is not obtained than random one.

Ex. in pharmaceutical industry sampling of tablet is carried out systematically. After every hundred tablet one tablet is pick up for analysis.

#### Disadvantages of nonrandom sampling:

- i) *It is biased or prejudiced.*
- ii) *Due to cyclic fluctuation in machine, whatever sample is withdrawn that may not be true or representative.*

#### 1.2.5 Sampling Techniques

##### a) Sampling of Liquids:

- *Care required for sampling of liquids*

- i) Cleanliness of apparatus and containers
- ii) Preservation of sample composition
- iii) Positive identification of samples
- iv) Care of sampling apparatus

▪ ***Preservation of sample composition:***

- i) If the sample contains solid particles or droplets of immiscible liquid, care must be taken such that all particles should transfer to sample containers.
- ii) Sample should not allow to solidify.
- iii) Dissolved and entrained gases should not allow to escape.
- iv) Entraining air in the outside should be avoided sample.
- v) During handling and transportation sample should be protected against breakage, *evaporation, leakage, exposure to sunlight and entry of dust and air.*

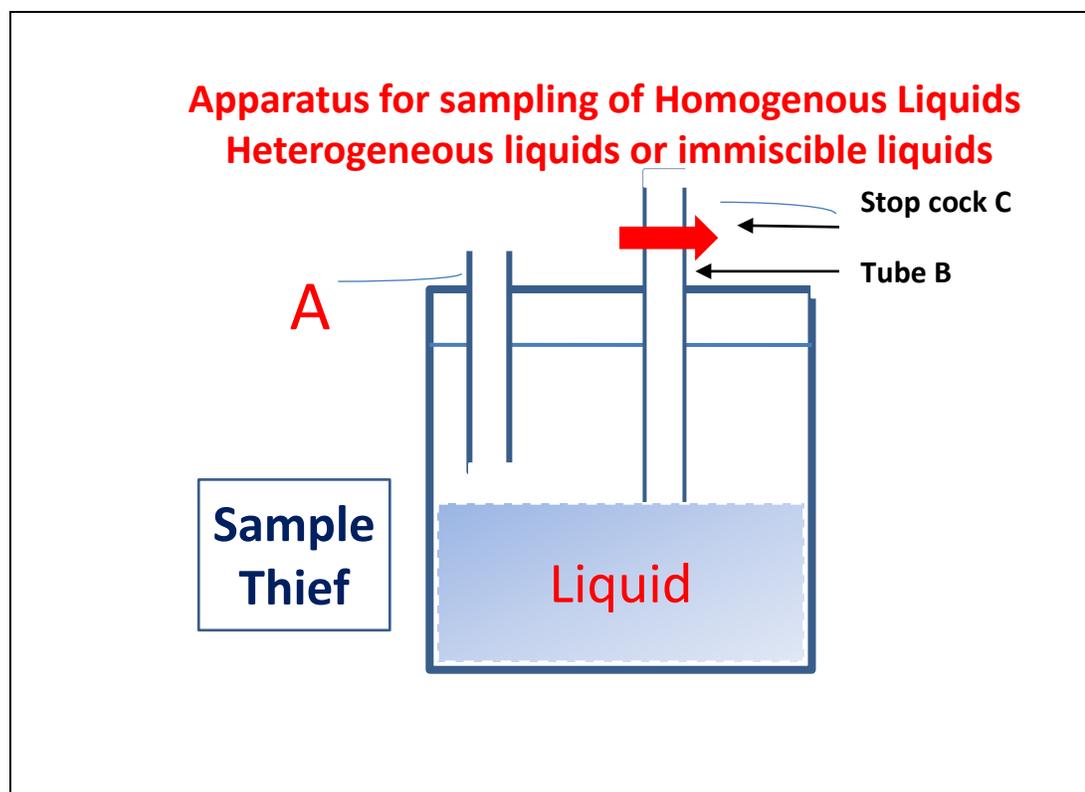
▪ ***Types of liquids to be sampled***

***Question: what are types of liquids for which sampling is carried out?***

- i) Homogenous Liquids
- ii) Heterogeneous liquids or immiscible liquids
- iii) Liquids containing Emulsions or unstable suspension
- iv) sampling of liquids containing partially crystallized solids
- v) Sampling of static and flowing liquids.
- vi) Sampling of liquids from various containers.

***Question: What is sample thief? How are homogenous and heterogenous liquids sampled?***

***(5 marks question)***



- Sample thief is sampling apparatus used for sampling of homogenous and heterogenous liquids.

Sample thief consist of glass bottle .The bottle is fitted with two tubes A&B. The tube A is open while the tube B is provided with stopcock C .The tube B must be longer than the height of the liquid in the container.

- **Sampling of Homogenous liquids:**

While collecting the sample the stopcock C is closed and then thief is lowered to desired depth in the container. Then stopcock C is opened, the liquid enters the bottle through A by displacing air through B. Then stopcock C is closed. The samples which are collected at different depths are then mixed to give gross sample.

- **Sampling of Heterogeneous liquids:**

In this if the liquid container is odd shaped, then the liquid is transferred to cylindrical or rectangular container.

The layers of liquids are identified; samples are taken from each layer by sample thief. While taking sample from each layer volumes of the sample taken must be in same ratio as the volumes of layers in the container. The individual samples are then mixed to give gross sample.

**Question: How the sampling of Emulsions and Suspensions and liquids containing partially crystallized solid are sampled?**

### Sampling of Emulsions and Suspensions:

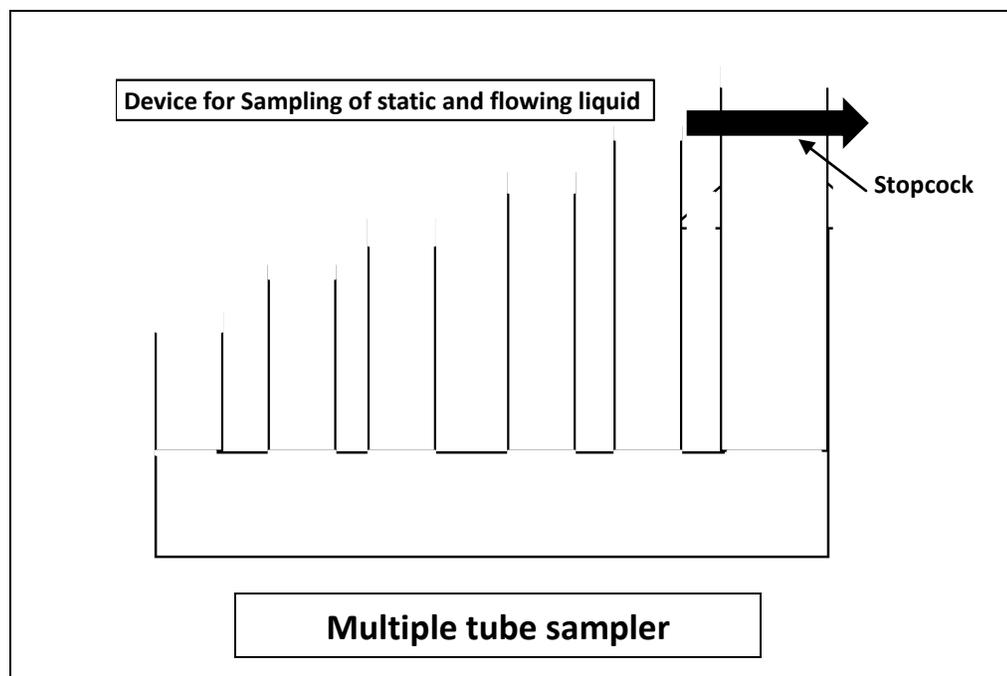
The two phases i.e. solids and liquids are separated by filtration. The two phases are weighed and then sample separately.

If the difficulties arise in the sampling then entire suspension is stirred to ensure uniform mixing and sampling is carried out as per the method use for sampling of immiscible liquids.

**Sampling of liquids containing partially crystallized solid:** The liquid are heated till solid dissolves in the liquid or melts in to a liquid. Then liquid is stirred and sampled as per the method used for Sampling of Emulsions and Suspensions:

### Sampling of static and flowing liquid:

The Sampling of static and flowing liquid are sampled using **multiple tube sampler** as shown in the following figure. Samples are taken at the centre of flow, as well as at different points from the centre of flow. Samples are collected at random. Samples are collected at random or at regular intervals. The individual samples are then mixed to give gross sample.



### b) Sampling of gases

**Question: What are various types of gases to be sample?**

- *Gases to be Sampled for analysis to know the composition*
  - i) *Gases from gas pipe line*
  - ii) *Gas from gas well*

iii) *Processing plants*

iv) *Storage holders such as tank*

v) *Open atmospheres*

▪ **Devices for sampling of gases :**

▪ *Gas sampling apparatus/device consist of following parts:*

i) **Sampling probe:** *Sampling line attached to container or vessel. It is injected into gas containers/pipe/well etc.*

ii) **Sample Container:** *Vessel in which gas sample is collected ; Size of containers may vary from 250cm<sup>3</sup> to several cubic meters.*

iii) **Mercury Trap:** *It is used to remove excess of gas.*

iv) **Vacuum Pump:** *The container is connected to pump for vacuumisation.*

**Question: Describe the general procedure used for sampling gases?**

i) **General procedures for sampling of gases**

ii) *Sample containers to hold the gas should be of glass*

iii) *The containers are connected to stopcock at both ends which will facilitate easy flushing.*

iv) *The joints are made from glass to make container leak proof.*

v) *Rubber tubing should be avoided to avoid the reaction.*

vi) *The stopcock are carefully cleaned and then lubricated every time before every time.*

vii) *The analysis of gas sample should be carried out simultaneously or immediately, after the sampling .*

viii) *Flushing, displacement by liquid and expansion into evacuated vessel are general methods used for sampling of gases.*

ix) *In flushing method, the sample container should be flushed with the gas to be sampled ten to fifteen times.*

**Question: Write notes on ambient sampling**

***Ambient sampling: Sampling of air is called as ambient sampling.***

i) *The definite area is selected for sampling.*

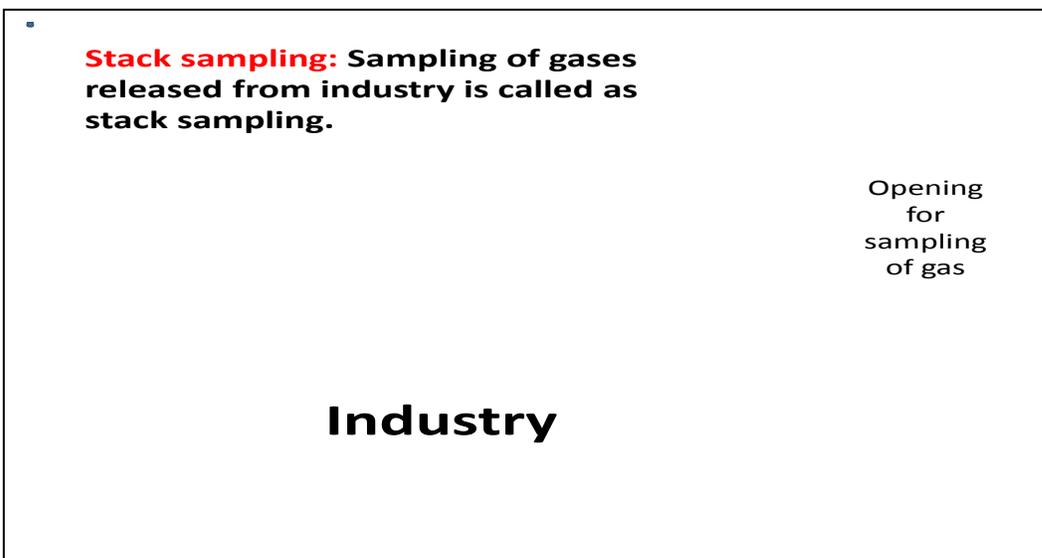
ii) *Sampling stations are decided are on the basis of grid pattern.*

iii) *Ambient sampling is difficult as the composition of air depends on wind velocity, wind direction, temperature, height, and season. These variables changes from time to time and place to place.*

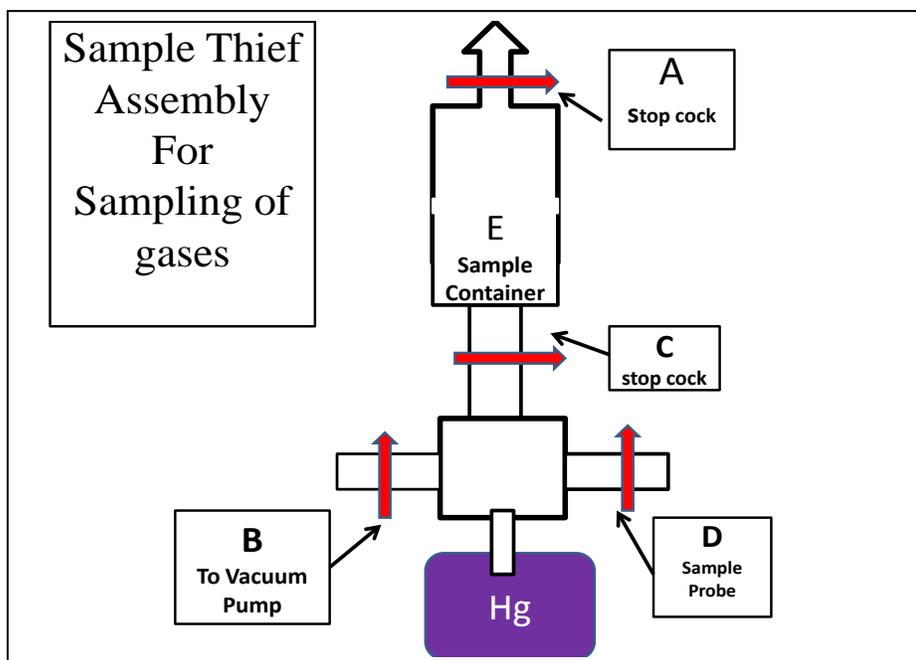
- iv) Sampling of atmospheric gases should be carried out region wise and area wise and time wise.
- v) As atmospheric gases contains particulate matter, smoke, dust etc, the atmospheric air is passed through series of filters ,series of trapping solutions and then collected.
- vi) For the collection of atmospheric air, plastic bags of different sizes, bottles, glass containers metal containers with fluid displacement pump are used.
- vii) The most widely used apparatus is gas sample thief.

**Stack Sampling:**

- i) The industrial gases are generally sampled continuously
- ii) Sample collected should represent a constant fraction of the total flow and all portions of stream are sampled
- iii) Sampling of gases is carried out by sample thief.



- ***Sampling of Gases:***
- *Two methods are used*
- *i) Static method*
- *Ii) Dynamic method*
- ***The apparatus for sampling of gases***



i) **Static method or Evacuation Method:** Sample container is evacuated by means of vacuum pump.

For evacuation stopcocks B & C are kept open and stopcocks A & D are kept closed.

After evacuation the container is also warmed to remove adsorbed gases on wall of the container. Then stopcock A and B are closed, C and D are open. The gas to be sampled is allowed to enter into sample container through sample probe D. The excess of gas escapes and is immersed in a pool of mercury. The evacuation and filling is carried out repeatedly to get desired sample.

- **Use:** This method is useful when small amount of gas is available

ii) **Dynamic method or Flushing method:** In this method, sample container is not evacuated. Stopcock B is closed and A, C, D are kept open. Gas from the cylinder is allowed to flow at a steady rate into sample container. Flowing is continued for some time to remove any residual gas from the sample container. The sample is isolated by closing stopcock A, C, D.

**Use:** This method is useful when large amount of gas is available

c) **Sampling of Solids:**

**Question:** What is meant by bulk ratio and size to weight ratio? Explain importance of these in sampling?

In the sampling of solids the concept of bulk ratio is important.

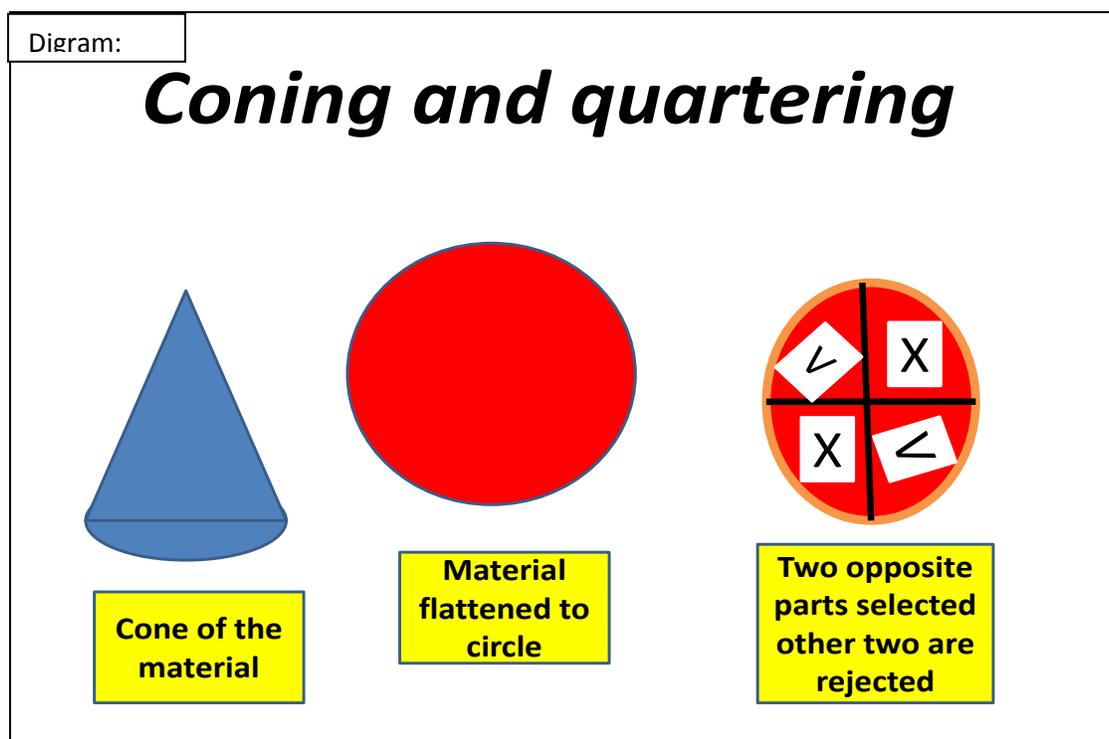
- $\text{BULK RATIO} = \frac{\text{Weight Of The Sample}}{\text{Total weight of Bulk material}}$
- Another parameter introduced in the case of heterogeneous materials is size to weight ratio ;
- $\text{SIZE TO WEIGHT RATIO} = \frac{\text{weight of the largest}}{\text{Weight of the sample}}$
- This concept is applied to determine the number and size of increment.

*For sample which is true representative of bulk material bulk ratio of the sample is large and size to weight ratio should be small*

*Question: Describe / explain different methods use for reduction of sample size?*

#### Reduction of Sample Size:

- Coning and quartering:** Gross sample is crushed to suitable mesh size and pile into conical shape .Pile is then flattened and divided into quarters. Opposite quarters are taken, other two are rejected. Process is repeated until suitable sample is obtained.



- Tabling rolling and quartering:** Sample is uniformly spread on square polythene sheet placed on a table. Material available on table is mixed by carefully by lifting one end of polythene sheet pulling towards opposite end of sheet ,this process makes particles rollover one another.

The steps are repeated to obtain homogenous mixture. The mixture is then spread into a disc on polythene sheet. The disc is divided into four quarters, two opposite quarters are rejected. Process is repeated until suitable sample is obtained.

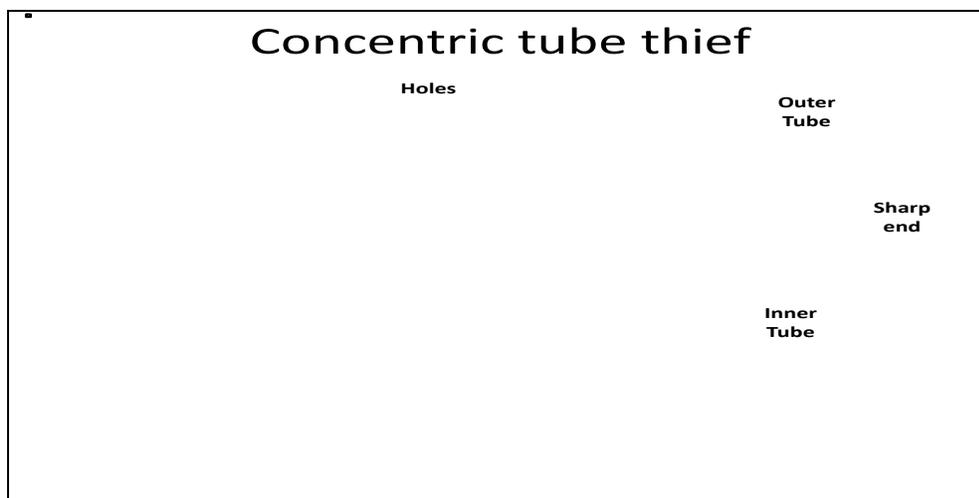
**Question: Explain the use of concentric tube thief in sampling? (Explain with diagram)**

**Sampling of Particulate Solids:**

i) **Concentric tube thief:** It is used to take samples of free flowing materials.

Ex. finely divided ores, cement, powder and granular material.

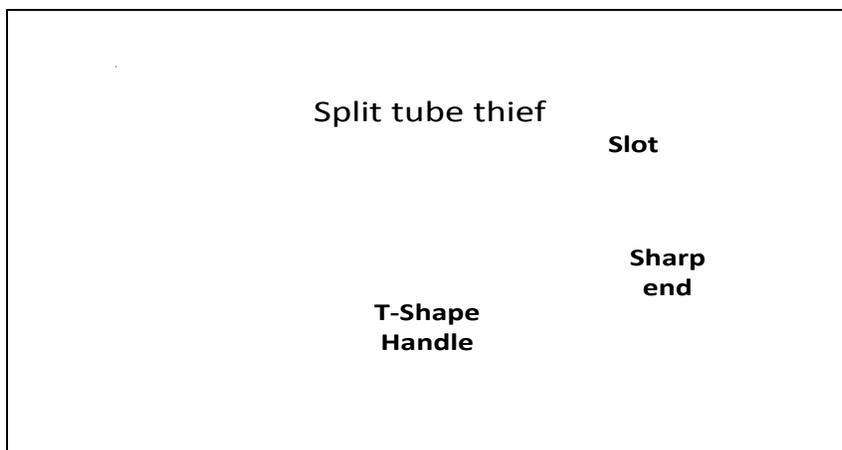
It consists of two concentric tubes one fitting closely inside other. The inner tube can be rotated inside the other tube. The outer tube can be pointed and pierce a container; both tubes have holes cut into them in corresponding positions to remove a sample. The inner tube is rotated so that the holes on it are closed and the thief is inserted in to container. When the thief has reached to appropriate position the inner tube is rotated to open the holes and material gets in to it; it is then closed before withdrawing the thief from the container. **Diagram:**



**Question: Explain the use of Split tube thief in sampling?(Explain with diagram)**

**Split tube thief:**

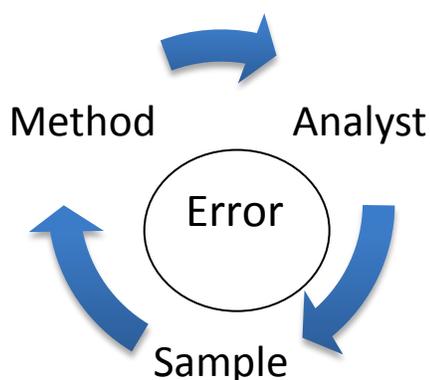
It consists of metallic tube with slot, running the entire length of the tube. The tube is having sharp end. It has T-shaped handle fixed at one end. The thief is pierced into container through its sharp end. When it reaches the desired point, the slot gets filled with the sample. The thief is withdrawn



**Question: How sampling of particulate solid is carried out? 5 marks question (Explain concentric tube thief and Split tube thief with diagram)**

### 1.3. Results of Analysis

Any analytical measurement involves the interaction of following three components. If any of this is not working proper that will results into error.



#### 1.3.1. Replicate Determinations :

The number of parallel determinations carried out known as *replicate determinations*. Determination of the number of times a measurement should be replicated in order to approach the value of experimental mean around the true mean with a certain degree of probability.

#### 1.3.2 Errors:

The word “error” has a very specific meaning in science: error is simply the difference between an observed result and the “true,” “actual,” “known,” or “accepted” value. It is a way of expressing accuracy, or how close a measurement is to the “true” value. Error can be reported several ways.

### 1.3.3 Types of error

- i) Determinate error
- ii) Indeterminate or random Error
- iii) Gross error

### 1.3.4 Determinate or systematic error :

Determinate error are those for which source can be observed or detected.

Determinate error can be located, measured and accounted.

***A common cause of determinate error is instrumental or procedural bias.***

For example: a wrong calibrated scale or instrument, a color-blind observer matching colors.

Another cause is an outright experimental blunder.

Determinate errors can be more serious than indeterminate errors for three reasons.

(1) There is no sure method for discovering and identifying them just by looking at the experimental data.

(2) Their effects cannot be reduced by averaging repeated measurements.

(3) A determinate error has the same size and sign for each measurement in a set of repeated measurements, so there is no opportunity for positive and negative errors to offset each other

### 1.3.5. Indeterminate or random error:

**The error are for which source cannot be observed or not detected or can be pinpointed.**

OR

**Indeterminate error is the errors which can be located, measured and accounted for.**

It causes measurements to fluctuate (vary slightly high and low) around the true value.

- This type of error has no assignable source and cannot be eliminated, but it can be understood mathematically
- Ex. Flying of ppt. in gravimetric analysis

***Distinguish between Determinate and error Indeterminate Error***

Sr.	Characteristics	Determinate	Indeterminate Error
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No.		error	
1	<b>Origin</b>	Source can be observed	No Source can be observed
2	<b>Magnitude</b>	Large	Small
3	<b>Direction</b>	Unidirectional	No direction
4	<b>Reproducibility</b>	Reproducible	Not Reproducible
5	<b>Effect</b>	Affect the measurement	No Affect on measurement
6	<b>Remedy</b>	Minimization possible, elimination in some cases possible	No elimination

**1.3.5. Gross Error:** This type of error occur due to a fault or blunder on the part of analyst.

- Analyst is responsible for this type of error.
- Ex. Preparation of solution in ordinary tap water.
- Unwashed/dirty/ glass ware used for expt.
- Forget to add indicator in the titrand

### 1.3.6 Classification of Determinate error :

Determinate error is classified into four types on the basis of their sources.

- Instrumental errors:
- Methodic errors
- Personal error
- Operational error

#### **Instrumental errors:**

The errors which arise due to poorer /wrong calibration of measuring devices such as pipette, burette, balance, weights instrumental techniques such as conductivity meter, potentiometer  
Uncertainty in the last digit of the measurement due to least count of the instrument or volumetric glass ware.

Ex.a) In volumetric analysis if 10 ml of pipette delivers 10.1 ml of liquid then the error introduced is 1%.

b) Counting /noting burette reading

c) Improper response: Optimum condition for the working of the Instrument. Instrument works in that condition only.

Ex. Working of glass electrode to measure pH using pH meter.

pH of solution 1-10 can be recorded properly. If the solution is having pH greater than this range electrode system will give improper response

**Methodic Errors:** The errors arise due to inherent limitations & drawbacks of procedure employed for analysis are known as methodic error.**Ex.**

- i) In gravimetric analysis of ppt. is Soluble due to improper pH condition.
- ii) In volumetric analysis if excess amount of titrant is added after equivalence point to get desired colour change, this error occurs due to extra drop is called as titration error.
- iii) This type of errors can be eliminated by using method of analysis.

***These types of errors obtained due to classical methods as these methods involves no. of steps.***

***.Operational errors:*** The errors obtained due to incompleteness in steps involved in analysis or due to insufficient knowledge / mishandling of the instruments are called as Operational errors.

***Examples***

- i) Weighing of the hot crucible during gravimetric analysis.
- ii) Loss of precipitate during filtration during gravimetric analysis.
- iii) Blowing of last drop of in the nozzle of the pipette
- iv) Improper recording of the instrument
- v) Under washing or over washing of the ppt during gravimetric analysis.
- vi) Ignorance of temp. for a particular reaction.

**Personal error:** The error arises due to lack of skill ,expertise and physical limitation of the analyst are known as Personal error:

- Ex. a) Due Colorblindness the person unable to detect end point .
- b) Blowing of last drop of liquid being delivered by pipette.

### **1.3.6. Minimization of errors :**

- i) Calibration of apparatus and Instruments: Operational and instrumental error can be minimized .
- ii) Running Blank determination : Methodic and operational errors can be minimized
- iii) Use of Independent method of analysis: Analysis of same sample by two method of analysis ,one which will be chosen & results obtained can be compared. Methodic and operational errors can be different

- iv) Running control determination: Standard sub. Analyzed and its result compared with the true value, Deviation of the obtained result from the true or expected value will be measure of Methodic and operational errors
- v) Running Parallel determination: Analysis of same sample by two different method by same analyst, or different. Methodic error will differ in two cases, if same analyst Methodic and personal error will be differ in two cases if different analyst.
  - Standard addition method : Sample is analyzed alone then sample + standard substance analyzed Methodic and operational errors will be same for two measurements
  - Internal standard method: Fixed amount of reference material is added to all standard solutions, blank and sample. Ex. Na is added in the analysis of soil while determining lithium
  - Amplification method: detector signals are amplified to rectify the improper response of detector.

***With the knowledge of type of error analyst can modify existing method, type of error and magnitude.***

***Accuracy & Precision:***

**Accuracy: It can be defined as closeness of the observed value to the true or accepted value.**

- Accuracy for single measurement is judged in terms of absolute and relative error

***a) Absolute Error:***

Absolute error =  $(x_i) - (x_t)$ . Where  $x_i$  = observed result and  $(x_t)$  is true value

The formula is used this way consistently so that the meaning of the sign of the error is clear: positive error means the observed result is too large, while negative error means the measured result is smaller than true

***b) Relative Error***

Relative error compares the size of an error to the value of the true measurement. Thus,

$$\text{Relative error} = \frac{x_i - x_t}{x_t}$$

Relative Error = (observed result – true result)/true value.

Relative error can be expressed as a decimal, percentage, parts per thousand, parts per million, etc.

$5/25 = 0.08$  decimal equivalent of relative error

$(2/25) \times 100 = 8\%$  percentage relative error

$(2/25) \times 1,000 = 80$  ppt parts per thousand relative error

Sr.No	Parameter	Accuracy	Precision
1	Defination	Closeness of a measured value with true or accepted value	Agreement amongst the observation
2	Indicator	Reliability of method	Reproducibility of method
3	Measure	Measured in terms of absolute and relative error	Standard deviation is the measure of the precision
4	Evaluation	Evaluated for single observation	Evaluated for set of observation
5	Calculation	Can be calculated if true or accepted value is known	No need to know true or accepted value is
6	Relation between Accuracy & Precision	Good degree of accuracy accompanied by good precision	Good precision can not guarantee good precision accuracy

1.3.7 **Precision:** It can be defined as Agreement amongst the observation.

It is the numerical difference without regard to sign between an observation and the mean or the median for the set of values that includes the value.

Reproducibility is measured in terms of precision.

**Precision can be expressed by**

i) **Mean :** The *mean* is the most widely used measure of the central value. It is denoted by  $\bar{x}$

$$\bar{x} = \frac{x_1 + x_2 + x_3 + x_4 + x_n \dots \dots}{N}$$

ii) **Median:**

When quick measure of central value is to be decided and when gross errors are suspected the central tendency of a group of results can be expressed in terms of *median*.

If *N* no of observations are arranged in either in ascending or descending order, the middle observation when 'N' is odd or the mean of two middle observation when N is even is known as median.

Ex. 1) 10.3,10.4, 10.5,10.7,10.8 (odd number of total observation the median is middle value i.e. 10.5)

2) 10.2, 10.3, 10.4, 10.5, 10.7, 10.8 ( even number of total observation, the median is average of the middle pair of observations i.e. 10.45).

**iii) Mode:**

The observation which occurs most frequently (i.e. which is repeated maximum number of times) in a series of observations is known as *mode*. It is yet another quick measure of central value if the number of observations is not too small.

**For example, the mode of the set of data: 12,6, 12,7, 12,9, 12,7, 12,6, 12,8, 13,0, 12,5, 12,6, the value 12.6 is the mode since this is occurring with maximum frequency (three times).**

**iv) Range (Spread):**

The difference between the largest and smallest values in a set of measurements is *known as the range*.

It tells the spread of data. The range is often used, with appropriate factors that depend on the number of measurements, as a quick statistics to a rough estimate of precision.

**v) Absolute Deviation:**

The error of a measurement cannot be stated if the true value of the quantity is not known. It is meaningful then to take the difference between a particular measured value (observation) and the arithmetical mean of a series of measurements and this difference is called as its *deviation for apparent error*.

**OR**

**Difference between particular measured value (observation) and the arithmetical mean is called as deviation.**

**A deviation is generally taken without regard to sign. It is defined mathematically as,**

$$d = xi - \bar{x}$$

**vi) Relative Deviation:**  $= \frac{\text{deviation}}{\text{mean}} = \frac{d}{\bar{x}}$

**vii) Average Deviation:** *It is the ratio of sum of the absolute deviations to the number of deviation*

The average deviation (a.d.) or the mean deviation is the average of individual deviations:

$$\bar{d} = \frac{d1 + d2 + d3 + d4 + dn \dots}{N}$$

**viii) Relative Average Deviation:**

The ratio of the average deviation to the mean is known as *Relative Average Deviation* (RAD) which can be expressed as *percent average deviation* when multiplied by 100, thousand average deviations when multiplied by 1000.

$$R. A. D = \frac{\text{average deviation}}{\bar{x}} = \frac{\bar{d}}{\bar{x}}$$

$$R. A. D = \frac{\text{average deviation}}{x} \times 100$$

$$R. A. D = \frac{\text{average deviation}}{\bar{x}} \times 1000$$

### ix) Standard Deviation:

Standard deviation is the most important statistic to indicate the precision of an analysis. According to the International Union of Pure and Applied Chemistry (IUPAC) the symbol  $\sigma$  is used for population standard deviation and the symbol  $S$  is used for sample standard deviation.

*It is defined as the square root of the mean of the squares of individual deviations.*

*Mathematically;*

If N is less than 20  $\text{Standard deviation}(S) = \frac{\sqrt{\sum(x_i - \bar{x})^2}}{N-1}$

If N is greater than 20  $\text{Standard deviation}(S) = \frac{\sqrt{\sum(x_i - \bar{x})^2}}{N}$

x) **Variance:** Square of standard deviation is called as Variance.

$$\text{Variance} = S^2$$

x) **Coefficient of Variation: Ratio of standard deviation to mean, and it's expressed as percentage**

$$C. O. V. = \frac{S}{\bar{x}} \times 100$$