

Introduction to Volumetric Analysis

S.Y. B.Sc. Semester – IV
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2. Methods of expressing concentrations
3. Primary and secondary standard solutions
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Introduction

- Chemical analysis plays an important role in study of composition or constituents of substances or material.
- The chemical analysis is broadly divided into two types
 - Qualitative analysis
 - Quantitative analysis

- The volumetric method involves measurement of volumes of the reacting substances.
- The weight of the required constituents is indirectly obtained by measuring the volume of a solution of known composition required to react with a known volume of a solution containing an unknown weight of the desired constituent.
- This is done by a process known as titration which is divided into four types depending upon the nature of the chemical reaction. The four types are
 - a. Acid – base or neutralization methods**
 - b. Precipitation methods**
 - c. Complexometric methods**
 - d. Oxidation – reduction methods**

- The quantitative analysis is further classified into two branches namely
 - **Volumetric analysis**
 - Gravimetric analysis

Volumetric analysis

- Volumetric analysis is also known as titrimetric analysis.
- The reagent (the titrant) is added gradually or stepwise to the analyte from a burette.
- The key to performing a successful titrimetric analysis is to recognize the equivalence point of the titration (the point at which the quantities of the two reacting species are equivalent), typically observed as a colour change.
- If no spontaneous colour change occurs during the titration, a small amount of a chemical indicator is added to the analyte prior to the titration.
- Chemical indicators are available that change colour at or near the equivalence point of acid-base, oxidation-reduction, complexation, and precipitation titrations.
- The volume of added titrant corresponding to the indicator colour change is the end point of the titration.
- The end point is used as an approximation of the equivalence point and is employed, with the known concentration of the titrant, to calculate the amount or concentration of the analyte.

<https://www.youtube.com/watch?v=Iurzrzwm9Fo>

<https://www.youtube.com/watch?v=d1XTOsnNIgg>

<https://www.youtube.com/watch?v=wRAo-M8xBHM>

<https://www.youtube.com/watch?v=YIYJr6WlfHA>

- In volumetric analysis, **concentration** of substances are found out by volume determination.
- The unit used for measurement of volume of a liquid or solution is "litre".
- *The litre is defined as the 'volume occupied by one kilogram of water at the temperature of its maximum density (4°C) and at normal atmospheric pressure'.*

- The millilitre is the thousandth part of a litre.
- The cubic centimeter (cm^3) is the volume occupied by a cube such that each edge of the cube is one centimeter in length.
- The relationship between millilitre and cubic centimeter is
$$1000 \text{ ml} = 1000.028 \text{ cc}$$
- The term ml is more correct

- The precision of volumetric work depends upon accuracy with which volume of liquids can be measured.

- There are certain sources of errors which must be carefully considered.
 - Changes in temperature cause change in the volume of glass apparatus and liquids.
eg. An ordinary glass flask of 1000ml volume shows an increase of in capacity 0.025ml per degree centigrade.
 - There may be errors of calibration of the apparatus
eg. the volume marked on the apparatus may not be the true volume.
- Such errors can be eliminated only by recalibrating the apparatus

Methods of Expressing Concentration of solutions

There are many systems of expressing the concentration of solutions.

- Weight of solute present in a given volume of solution
- Moles of solute present in one litre of solution, called molarity
- Gram equivalents of solute present in one litre of solution, called normality
- Percentage of solute by weight in a solution of known specific gravity

1. **Weight of Solute per Unit Volume of Solution**

In preparation of solution using this system, a known weight of the solute is dissolved and diluted to known volume.

If accuracy is required, the solute is weighed and transferred to a volumetric flask, and diluted to a known volume.

The concentration is usually expressed as grams of solute per millilitre of solution.

Any multiple or fractional part of such solution will contain a known weight of solute.

2. Molarity

- a. **A mole** : The molecular weight expressed in grams of any substance is called as mole or gram molecule of the substance. For example, sodium chloride has molecular weight 58.5g of sodium chloride means one mole of it.
- b. **Millimole** : The mole is very large unit, hence a smaller unit which is one thousandth of it, known as millimole is used. Thus 1 mole = 1000 millimoles.
- c. **Molar Solution** : A molar solution is defined as the solution containing one mole of the solute in a litre of its solution. For example 40g of NaOH in one litre of solution is called as 1M NaOH solution

$$\text{Number of Moles} = \frac{\text{Weight of solute in grams}}{\text{Molecular weight of the solute}}$$

Molarity of Solution : It is defined as the number of moles of the solute present in one litre of its solution. It can also be defined as number of millimoles of a solute present in one millilitre of its solution.

$$\text{Molarity} = \frac{\text{Number of moles of the solute}}{\text{Volume of the solution in litre}}$$

$$\text{Number of moles} = \text{Molarity} \times \text{Litre}$$

$$\text{Molarity} = \frac{\text{Number of millimoles of the solute}}{\text{Volume of the solution in millilitre}}$$

$$\text{Number of millimoles} = \text{Molarity} \times \text{MilliLitres}$$

3. Normality

The concentration of solution can also be expressed in terms of normality.

Various terms involved in it are -

Equivalent Weight :

The equivalent weight of a substance (element or compound) as:

"The number of parts by weight of it, that will combine with or displace directly or indirectly 1.008 parts by weight of hydrogen, 8 parts by weight of oxygen, 35.5 parts by weight chlorine or the equivalent parts by weight of another element".

- **Milliequivalent Weight** : It is obtained by dividing the equivalent weight by 1000.

- **Gram Equivalent Weight** : It is the equivalent weight expressed in grams

Equivalent weight of a substance = 1 equivalent of a substance = Equivalent weight of substance in grams

- **Milligram Equivalent Weight** : It is obtained by dividing the gram equivalent weight by 1000.

Normality of Solution : Normality is a system of expressing concentration based on number of equivalents of solute present in one litre of solution or the number of milliequivalents of solute present in one millilitre of a solution.

$$\text{Normality} = \frac{\text{Number of equivalents of the solute}}{\text{Volume of titration in litre}}$$

$$= \frac{\text{Number of milliequivalents of the solute}}{\text{Volume of the solution in millilitre}}$$

$$\text{Number of gram equivalents} = \text{Normality} \times \text{Litres}$$

- <https://www.youtube.com/watch?v=KLjWa9cE2uk>
(molarity made easy)
- https://www.youtube.com/watch?v=hQrih9m_nmQ
- https://www.youtube.com/watch?v=QCZMyx_557I
- <https://www.youtube.com/watch?v=fDh30u-c0Sc>
- <https://www.youtube.com/watch?v=0MwIMhcAWLQ>
(normality and equivalent weight)

Primary and Secondary Standard Solutions

- The standard solution is prepared by dissolving an accurately weighed quantity of a highly pure material called a primary standard and then diluting to an accurately known volume in a volumetric flask
- If material is not sufficiently pure then solution is prepared to give approximately the desired concentration and this standardized by titrating a weighed quantity of a primary standard.
- https://www.youtube.com/watch?v=xKH2AvS_s0k

- The primary standard should fulfill the below requirements
 - It should be 100% pure
 - It should be stable to drying temperatures and it should be stable indefinitely at room temperature. The primary standard is always dried before weighing.
 - It should be easily and readily available
 - Although not necessary it should have a high formula weight.
- This is so that a relatively large amount of it will have to be weighed to get enough to titrate.
- The relative error in weighing a greater amount of material will be smaller than that for small amount

- **Preparation of Standard Solution**

- In case of volumetric analysis, the final result depends upon the accuracy with which the standard solution is prepared.
- The concentration of standard solution is established by direct and indirect method.

- **Direct Method of Preparation of Standard Solution (Primary Standard)**

- In order to prepare a standard solution, the substance is weighed accurately equal to an equivalent, or a definite fraction or multiple of an equivalent, dissolved in water and diluted to a known volume.

- **Indirect Method of Preparation of Standard Solution (Secondary Standard)**

- The process of determining the concentration of a solution by titrating it against a solution of a pure substance of known concentration is called as standardization.
- Thus the exact concentration of the secondary standard solution is determined by titrating it against a primary standard solution.
- The secondary standard solution may be further used for standardization of other solutions.

Equivalent weight in different types of reactions

- There are various types of chemical reactions. The equivalent weight varies with the type of reaction.
- Same compounds may have different equivalent weights in different chemical reactions.
- Hence normality of a particle solution may also be different in different chemical reactions.

- Equivalent weight in different types of chemical reactions is discussed as shown below
 - Neutralization Reactions
 - Complex Formation and Precipitation Reactions
 - Oxidation – Reduction reactions

• Neutralization reactions

- In reactions between acids and bases, one equivalent is the weight of the reagent which contains or reacts with one gram atom of replaceable hydrogen (1.008g) or with one gram molecule of hydroxyl (17.008g).

$$\text{Equivalent weight of acid} = \frac{\text{Molecular weight of acid}}{\text{Basicity of that acid}}$$

- The **basicity** is defined as the number of replaceable hydrogen atoms present in one molecule of that acid.
- The term **acidity** is defined as the number of replaceable hydroxyl ions present in one molecule of that base

$$\text{Equivalent weight of acid} = \frac{\text{Molecular weight of base}}{\text{Acidity of that base}}$$

- **Complex Formation and Precipitation Reactions**

- The equivalent weight of complex formation and precipitation reactions is the weight of the substance that contains or reacts with 1g atom of a monovalent cation M^+ , $\frac{1}{2}$ g atom of bivalent cation M^{2+} , $\frac{1}{3}$ g atom of a trivalent cation M^{3+} and so on.
- The equivalent weight of cation is equal to its atomic weight divided by valency.

- The equivalent weight of a substance in complex formation reaction can be determined by writing down the ionic equation of the reaction



- Calibration
- Calibration of measuring instruments

- <https://lab-training.com/2015/01/06/volumetric-apparatus-use-calibration/>
- <https://pharmapathway.com/calibration-procedure-volumetric-glassware/>

ANALYTICAL CHEMISTRY

QUALITATIVE ANALYSIS

QUANTITATIVE ANALYSIS

CLASSICAL "WET" ANALYSIS

INSTRUMENTAL ANALYSIS

CLASSICAL "WET" ANALYSIS

QUALITATIVE INORGANIC - ORGANIC ANALYSIS

OPTICAL METHODS

SEPARATION METHODS

ELECTRO-ANALYTICAL METHODS

GRAVIMETRIC ANALYSIS

VOLUMETRIC ANALYSIS

Instrumental analysis

- Instrumental analysis is a field of analytical chemistry that investigates analytes using scientific instruments.
- Instrumental chemistry involves the use of complex machines within the field of analytical chemistry.
- This field uses instruments to analyze particles and molecules. Part of analytical chemistry is exploring how these instruments work within the framework of research.
- Two common methods of instrumentation are spectroscopy and mass spectrometry. Spectroscopy uses electromagnetic radiation, while mass spectrometry uses magnetic and electric fields.
- Instrumental chemistry is utilized within the food, pharmaceutical, medical and environmental industries.

- The instrumental methods of chemical analysis are divided into categories according to the property of the analyte that is to be measured.
- Many of the methods can be used for both qualitative and quantitative analysis.
- The major categories of instrumental methods are the **spectral, electroanalytical and separatory**.

- The possibility to realise analyses on small and very small samples is one of advantages of instrumental methods in comparison with chemical methods.
- Both chemical and instrumental analysis methods have a series of limitation, every of them having advantages and disadvantages

Advantages of Instrumental methods of analysis

- UV visible spectrometry a small amount of the sample is required for analysis
- Determination by instrumental method is considerably fast
- Complex mixture can be analyzed either with or without their separation
- Reliability and accuracy of results are obtained by instrumental method
- When non-instrumental method is not possible, instrumental method is the only answer to the problem

Limitations of Instrumental methods of analysis

- In general instrumental methods are costly
- Require maintenance
- Also require trained personnel for handling
- The sensitivity and accuracy depend upon the type of the instrument
- Specialized training for handling instrument is required
- There is frequent need of checking results with other methods
- In some cases instrumental method may not be specific

List of Instrumental methods of analysis

- UV visible spectrometry
- IR spectrometry
- Atomic Absorption spectrophotometry (AAS)
- Nuclear magnetic resonance spectrophotometry
- Emission spectroscopy
- Fluorometry
- Turbidimetry
- Conductometry
- Polarimetry
- Mass spectrometry
- Polarography
- Raman spectroscopy
- Flame photometry
- Radiochemical methods
- Potentiometry
- Electrogravimetry
- Nephelometry
- Refractometry
- X – ray diffraction method

Instrumental methods

Spectral	Electro- analytical	Separatory
<ul style="list-style-type: none">•Absoptiometry•Nuclear Magnetic Resonance•Thermal analysis•Infra Red•UV spectrophotometry•X-ray absorption•Turbidimetry•Nephelometry•Refractometry	<ul style="list-style-type: none">•Conductometry•Voltametry•Polarography•Electrogravimetry•Coulometry•Amperometry•Potentiometry	<ul style="list-style-type: none">•Chromatography•Mass spectrometry

Non instrumental analysis

- The chemical methods (gravimetric and titrimetric) from ensemble of quantitative analysis methods are corresponding to macro scale determinations while instrumental methods are used for quantitative determinations starting with semi-microscale.

Chemical methods (Non instrumental analysis)

The chemical methods have advantages:

- The necessary equipment is very expensive;
- The methods are based on absolute measurements;
- Procedures are simple and precise

The chemical methods have disadvantages:

- The precision decrease with decrease of sample amount;
- The realisation of an analysis is realised in a enough long time period;
- They aren't flexible;
- They are pollutant for environment;
- Sometimes they aren't specific