

## QUANTITATIVE VOLUMETRIC ANALYSIS

**Volumetric analysis** is a general term for a method in quantitative chemical analysis in which the amount of a substance is determined by the measurement of the volume that the substance occupies. It is commonly used to determine the unknown concentration of a known reactant. Volumetric analysis is often referred to as titration.

### Acid-Base Titration

#### What is the meaning of Titration?

Titration is a common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of a known reactant. Because volume measurements play a key role in titration, it is also known as volumetric analysis.

A **reagent**, called the titrant or titrator,[1] of a known concentration (a standard solution) and volume is used to react with a solution of the analyte or titrant,[2] whose concentration is not known. Using a calibrated burette or chemistry pipetting syringe to add the titrant.

\* A **primary standard solution** is a highly purified compound that serve as a reference material in all volumetric titrimetric methods.

Important requirements for a primary standard are:

1-High purify.

2- To be of high stability and not affected or interact in one way or another under normal weather conditions.

3-Ready availability at modest cost.

4-Reasonable solubility in the titration medium.

5-Reasonable large molar mass so that the relative error associated with weighing the standard is minimized.

It is possible to determine the exact amount that has been consumed when the endpoint is reached.

**The endpoint** is the point at which the titration is complete, as determined by an indicator. This is ideally the same volume as the equivalence point, **the volume of added titrant at which the number of moles of titrant is equal to the number of moles of analyte.**

For example: - in the classic strong acid-strong base titration, the endpoint of a titration is the point at which the pH of the reactant is just about equal to 7, and often when the solution takes on a persisting solid color as in the pink of phenolphthalein indicator. There are however many different types of titrations.

Many methods can be used to indicate the endpoint of a reaction; titrations often use visual indicators (the reactant mixture changes color). In simple acid-base titrations a pH indicator may be used, such

as phenolphthalein, which becomes pink when a certain pH (about 8.2) is reached or exceeded. Another example is methyl orange, which is red in acids and yellow in alkali solutions.

Not every titration requires an indicator. In some cases, either the reactants or the products are strongly colored and can serve as the "indicator". For example, a redox titration using potassium permanganate (pink/purple) as the titrant does not require an indicator. When the titrant is reduced, it turns colorless. After the equivalence point, there is excess titrant present. The equivalence point is identified from the first faint persisting pink color (due to an excess of permanganate) in the solution being titrated.

### Types of titrations

There are various sorts of titrations whose goals are different to the others. The most common types of titrations in qualitative work are acid-base titrations, redox titrations, complexometric titration and precipitation titration.

#### 1- Acid-base titration

These titrations are based on the neutralization reaction that occurs between an acid and a base, when mixed in solution. The acid is added to a burette which was rinsed with the same acid prior to this addition to prevent contamination or diluting of the acid being measured. The base is added to a volumetric flask which had been rinsed with distilled water prior to the addition to prevent contamination or dilution of the base/alkali being measured. The solution in the volumetric flask is often a standard solution (one whose concentration is exactly known). The solution in the burette, however, is the solution whose concentration is to be determined by titration. The indicator used for such an acid-base titration often depends on the nature of the constituents. Common indicators, their colours, and the pH range in which they change colour, are given in the table below, when more precise results are required, or when the titration constituents are a weak acid and a weak base, a pH meter or a conductance meter are used.

Sq.	Indicator	Color on Acidic Side	Range of Color Change (pH)	Color on Basic Side
1	Methyl Violet	Yellow	0.0- 1.6	Violet
2	Bromophenol Blue	Yellow	3.0- 4.6	Blue
3	Methyl Orange	Red	3.1- 4.4	Yellow
4	Methyl Red	Red	4.4- 6.2	Yellow
5	Litmus	Red	5.0- 8.0	Blue
6	Bromothymol Blue	Yellow	6.0- 7.6	Blue
7	Phenolphthalein	Colorless	8.3- 10.0	Pink
8	Alizarin Yellow	Yellow	10.1- 12.0	Red

## 2- Precipitation titration

Precipitation titration: is titration depend upon the combination of ions to form a simple precipitate. Mohr method is a method depend upon formation a colored precipitate for the determination of chloride ion.

A small quantity of potassium chromate ( $K_2CrO_4$ ) solution is added to serve as indicator. The first excess of titrant results in the formation of a red silver chromate precipitate which signal the end point.

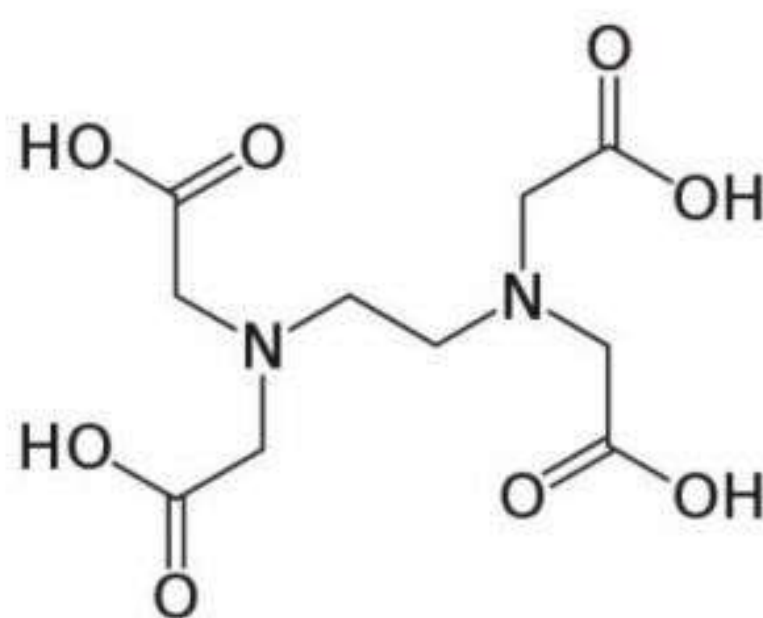
## 3-Redox titration

These titrations are based on a redox reaction between an oxidizing agent and a reducing agent. The oxidizing agent is added to the burette which was rinsed with the same oxidizing agent. The reducing agent is added to the conical flask, which had been rinsed with distilled water. Like in an acid-base titration, the standard solution is often the one in the conical flask, and the solution whose concentration is to be determined is the one in the burette.

Some redox titrations do not require an indicator, due to the intense colour of some of the constituents. For instance, in a titration where the oxidizing agent potassium permanganate (permanganometry) is present, a slight faint persisting pink colour signals the endpoint of the titration, and no particular indicator is therefore required.

## 4- Complexometric titration

These titrations are based on the formation of a complex between the analyte and the titrant. The chelating agent Ethylenediaminetetraacetic acid (EDTA) is very commonly used to titrate metal ions in solution. These titrations generally require specialized indicators that form weaker complexes with the analyte. A common example is Eriochrome Black T and murexide for the titration of calcium and magnesium ions.



Ethylenediaminetetraacetic acid (EDTA)

### Titrimetric analysis generally involve the following steps:

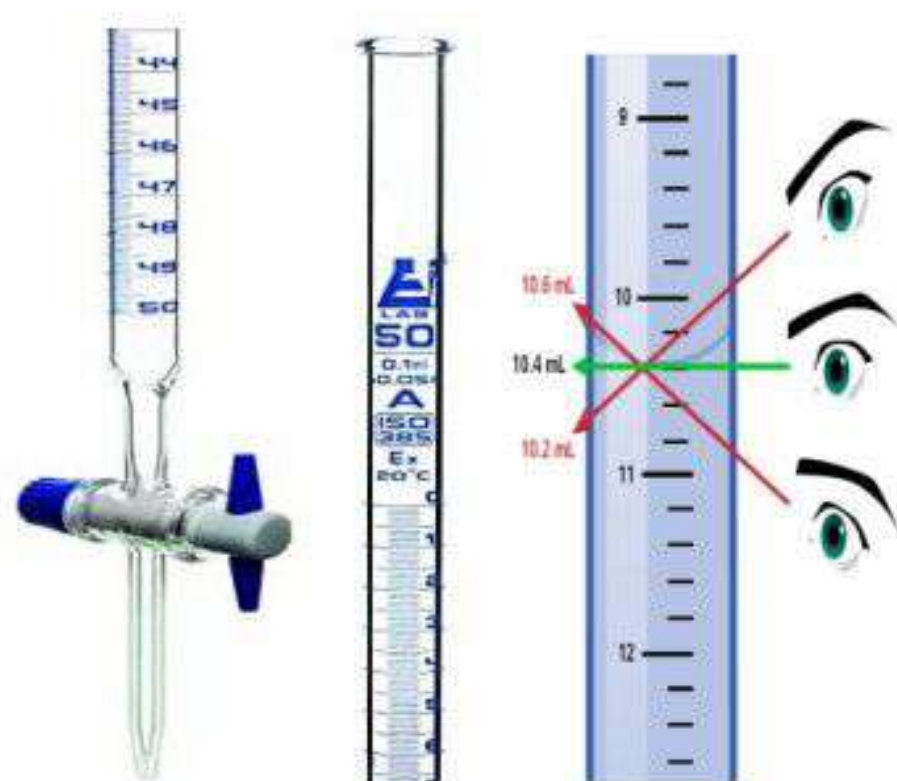
- Sampling
- Titrant preparation
- Standard preparation and conversion to a measurable form
- Titrant standardization by titration of an accurately known quantity of standard
- Sample preparation and conversion to a measurable form
- Sample titration with the titrant solution
- Data analysis

### Successful Titrimetric Analysis

#### A few rules of thumb for designing a successful titration are:

- The titrant should either be a standard or should be standardized.
- The reaction should proceed to a stable and well-defined equivalence point.
- The equivalence point must be able to be detected.
- The titrant's and sample's volume or mass must be accurately known.
- The reaction must proceed by a definite chemistry. There should be complicating side reactions.
- The reaction should be nearly complete at the equivalence point. In other words, chemical equilibrium favors products.
- The reaction rate should be fast enough to be practical.
- Substances of known purity for the preparation of standard solution.
- A visual indicator or an instrumental method detecting the completion of the reaction
- Calibrated measuring vessels, including burettes, pipettes, and measuring flasks as

follows:-



**Burette**



**Erlenmeyer flask (Conical flask)**



**Volumetric flask**

### Calculations of volumetric analysis:

**Standard solution** is one, which contains a known weight of the reagent in a definite volume of the solution.

**Molar solution** is one, which contains 1 gm molecular weight of the reagent per liter of solution.

$$M = \frac{\text{Weight}}{\text{M.Wt}} * \frac{1000}{\text{Volume(mL)}}$$

**Normal solution** is one that contains 1gm equivalent weight per liter of solution.

$$N = \frac{\text{Weight}}{\text{eq.wt}} * \frac{1000}{\text{Volume(mL)}}$$

**Part per million(ppm):** Milligrams of solute per liter of solution.

$$\text{ppm} = \frac{\text{weight solute(mg)}}{\text{Volume solution(L)}}$$

$$\text{ppm} = \frac{\text{wt(g)}}{\text{V(mL)}} \times 10^6$$

$$\text{ppm} = M \times \text{M.wt} \times 1000$$

For titrimetric reaction:



At equivalent point:

no.mmol of titrant(A)= no.mmol of titrand(B)

$$N_A \times V_A = N_B \times V_B$$

or

$$M_A \times V_A = M_B \times V_B \quad (R=b/a)$$