# T.Y.B.SC. (SEM-V) C-503-UNIT-5-CHAPTER-8 VOLUMETRIC ANALYSIS 


#### Abstract

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


## Volumetric Analysis(Titration)

## Titration :

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## SOME TERMS USED IN TITRATION

## Equivalence point (Veq):

The point in a titration where stoichiometrically equivalent amounts of analyte and titrant react (theoritical end of titration).

## End point (Vep):

The point of titration at which the completion of a reaction is practically observed Unfortunately, the endpoint and the equivalence point are not exactly the same.
The difference between the two is called the titration error.

## Titration error:

The difference between the end point and the equivalence point

$$
\mathrm{Et}=\mathrm{Vep}-\mathrm{Veq}
$$

## Titrant:

The standard solution of known concentration added from the burette.

## Analyte:

An unknown solution which is to be determined .

## Indicator:

A colored compound reagent added to the analyte solution to produce an observable physical change (usually change in color) at or near the equivalence point when the titration reaction is complete, and so mark the endpoint e.g: Phenolphthalein, Methyl Orange, Methyl red, etc.

## Back titration :

A technique used to determine the excess of a reagent used in the neutralization of the sample by a titration with a second reagent

## Standard solution:

A reagent of known concentration used to carry out a titrimetric analysis (titration).

## Primary standard:

Is a pure compound from which a standard solution of accurately known concentration can be prepared directly, without any need for standardization.

## Secondary standard:

Is a solution that its concentration is not accurately known so it is to be standardized by "Primary Standard" before use in titration.

## Standardization:

The process of finding the actual concentration of the secondary standard solution by titrating it with a suitable primary standard solution.

## REQUIREMENTS FOR THE PRIMARY STANDARD MATERIAL

1. Highest purity
2. Atmospheric stability
3. High solubility
4. High formula weight
5. Easily available at reasonable cost
6. Free from hydrated water so that the composition of the solid does not change with variations in humidity.

## Requirments of the standard solutions

1. Sufficiently Stable so its concentration is determined only once
2. React rapidly and completely with the analyte
3. Undergo a selective reaction with the analyte that can be described by a balanced equation.

## Types of volumetric titrations

i. Acid-base ( Neutralization) titration
ii. Precipitation titration
iii. Compleximetric titration
iv. Oxidation-reduction (redox) titration

## 1.Acid- Base titrations:

Many compounds, both inorganic and organic, are either acids or bases and can be titrated with a standard solution of a strong base or a strong acid. The end points of these titrations are easy to detect, either by means of an indicator or by following the change in pH using a pH meter.

## 2.Precipitation titrations:

In this type of titration, the titrant forms a precipitate with the analyte. An example is the titration of chloride ion with silver nitrate solution to form silver chloride precipitate. Again, indicators can be used to detect the end point,...
$\mathrm{Cl}^{-}+\mathrm{Ag}^{+} \quad \rightarrow \quad \mathrm{AgCl}(\mathrm{s})$ (white ppt)
$2 \mathrm{Ag}^{+}+\mathrm{K}_{2} \mathrm{CrO}_{4} \quad \rightarrow \quad \mathrm{Ag}_{2} \mathrm{CrO}_{4}$ ( brick red ppt)

## 3.Complexometric titrations:

In complexometric titrations, The titrant is often a chelating agent(Ligand) that forms a water-soluble complex with the analyte ( metal ion).
Ethylenediaminetetraacetic acid (EDTA) is one of the most useful chelating agents used for titration. It will react with a large number of elements, and the reaction can be controlled by the adjustment of the pH . Indicators can be used to form a highly colored complex with the metal ion.

## 4. Reduction-Oxidation (Redox) titrations:

The "redox" titrations involve the titration of an oxidizing agent with a reducing agent, or vice versa. An oxidizing agent gains electrons and a reducing agent loses electrons in a reaction between them.

## VOLUMETRIC (Titration) CALCULATIONS

No. of moles $A=\frac{\text { mass } A(g)\left(\frac{q}{m o l}\right)}{\text { Molar mass }}$
No. of moles $A=\operatorname{volume}(L) x$ Molarity of $A(m o l / L)$
No. of mmoles $\mathbf{A}=$ volume $(\mathrm{mL}) \times$ Molarity of $\mathbf{A}(\mathrm{mmol} / \mathrm{mL})$
mass of $\mathbf{A}(\mathrm{g})=$ No. of moles $\mathbf{x}$ Molar mass ( $\mathrm{g} / \mathrm{mol}$ )
Example 1:
Calculate the concentration of 100.0 mL of NaOH solution titrated to the end point with 75.8 mL of a 0.100 M standard solution of HCl .
$\mathrm{HCl}(\mathrm{aq})+\mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{NaCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
$\mathrm{na}=1 \quad \mathrm{nb}=1($ stiochiometric mole ratios of acid and base)
No of moles $=$ Molarity $(\mathbf{M}) \mathbf{x}$ volume $(\mathrm{L})$
No of mmoles $=$ Molarity $(\mathbf{M}) \mathbf{x}$ volume $(\mathbf{m L})$

$$
\begin{aligned}
& * * \quad \frac{\mathrm{M}_{\mathrm{a}} \mathrm{~V}_{\mathrm{a}}}{\mathrm{n}_{\mathrm{a}}}=\frac{\mathrm{M}_{\mathrm{b}} \mathrm{~V}_{\mathrm{b}}}{\mathrm{n}_{\mathrm{b}}} \\
& \frac{75.8 \times 0.10}{1}=\frac{C_{\mathrm{b} \times 100}}{1} \\
& \mathbf{M}_{\mathrm{b}}=\frac{75.8 \times 0.10}{100}=\mathbf{0 . 0 7 5 8} \mathbf{~ M}
\end{aligned}
$$

Example 2:
20 mL of $\mathrm{H}_{2} \mathrm{SO}_{4}(98 \mathrm{~g} / \mathrm{mol})$ was neutralized with 25 mL of 0.1 M sodium hydroxide solution. The equation of reaction is
$\mathbf{H}_{2} \mathrm{SO}_{4}+\mathbf{2 N a O H} \rightarrow \quad \mathrm{Na}_{2} \mathrm{SO}_{4}+\mathbf{2 H}_{2} \mathrm{O}$
Calculate (i) molar conc. of acid (M)
(ii) acid content of the solution in grams.

Solution:

$$
\begin{aligned}
& \frac{\mathrm{M}_{\mathrm{a}} V_{\mathrm{a}}}{\mathrm{n}_{\mathrm{a}}}=\frac{\mathrm{M}_{\mathrm{b}} \mathrm{~V}_{\mathrm{b}}}{\mathrm{n}_{\mathrm{b}}} \\
& \frac{M_{a} \times 20.0}{1}=\frac{0.10 \times 25}{2}
\end{aligned}
$$

Concentration of $\mathbf{H}_{2} \mathbf{S O}_{\mathbf{4}}\left(\mathrm{M}_{\mathrm{a}}\right)=\frac{1 \times 0.10 \times 25}{2 \times 20}=\mathbf{0 . 0 6 2 5} \mathbf{M}$
ii) mass of the acid in the solution ( $g$ )
mass $(\mathrm{g})=$ Molar conc.(Molarity) $\mathbf{x}$ Volume $(\mathrm{L}) \mathbf{x}$ Molar mass
mass $(\mathrm{g})=0.0625 \times\left(20 \times 10^{-3}\right) \mathrm{Lx} 98=0.1225 \mathrm{~g}$

## Example 3 :

A 18.50 mL of hydrochloric acid were neutralized by 25 mL of potassium hydroxide solution ( $56 \mathrm{~g} / \mathrm{mol}$ ) containing $7 \mathrm{~g} / \mathrm{liter}$. what is the molar concentration of the acid?

$$
\mathrm{HCl}+\mathrm{KOH} \quad \rightarrow \quad \mathrm{KCl}+\mathrm{H}_{2} \mathrm{O}
$$

Solution:
Given:
Molarity of $\mathrm{KOH}=\frac{\mathrm{wt}}{M \mathrm{w} t \times V(L)}=\frac{7 \mathrm{~g}}{\frac{56 g}{m o l} \times \mathbf{Z}}=\mathbf{0 . 1 2 5} \mathbf{M}$
$\frac{M_{\underline{a}} \underline{V}_{\underline{a}}}{n_{a}}=\frac{M_{\underline{b}} \underline{V_{b}}}{n_{b}}$
$\frac{M_{a} \underline{\times 18.5}}{1}=\frac{0.125 \times 25.0}{1}$
Concentration of $\mathbf{H C l}\left(\mathbf{M}_{\mathbf{a}}\right)=\frac{0.125 \times 25.0 \times 1}{18.5 \times 1}=\mathbf{0 . 1 6 9} \mathbf{~ M}$

## Example 4:

50.0 mL portion of HCl solution required 29.71 mL of $(0.019 \mathrm{M}) \mathrm{Ba}(\mathrm{OH})_{2}$ to reach an end point with bromocresol green indicator , Calculate the molarity of HCl .

## Solution:

$$
\begin{gathered}
\mathbf{B a}(\mathbf{O H})_{2}+2 \mathbf{H C l} \rightarrow \quad \mathbf{B a C l}_{2}+\mathbf{2 H}_{2} \mathbf{O} \\
\text { 1mole } \quad \text { 2 mole } \quad \text { 1mole } \\
\frac{\mathrm{M}_{\mathrm{Ba}(\mathrm{OH}) 2} \times \mathrm{V}_{\mathrm{Ba}(\mathrm{OH}) 2}}{1}=\frac{M_{\mathrm{HCl}} \times V_{\mathrm{HCl}}}{2} \\
\mathrm{M}_{\mathrm{HCl}}=\frac{2\left[\mathrm{M}_{\mathrm{Ba}(\mathrm{OH}) 2} \times \mathrm{V}_{\mathrm{Ba}(\mathrm{OH}) 2]}\right]}{V_{\mathrm{HCl}}} \\
\mathrm{M}_{\mathrm{HCl}}=\frac{2[0.019 \times 29.71]}{50}=0.023 \mathrm{M}
\end{gathered}
$$

