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 muroxide for the titration of calcium and magnesium ions.
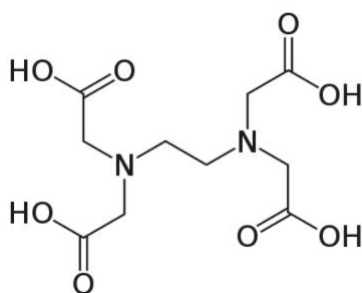
Ethylenediaminetetraacetic acid (EDTA)

**Titrimetric analysis generally in volve 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

followes:-
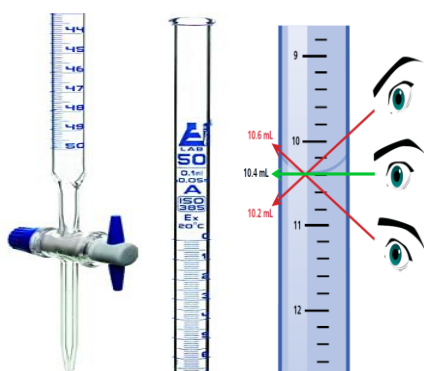
| **Burette** | **Erlenmeyer flask (Conical flask)** | **Volumetric flask** |

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.

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

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

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

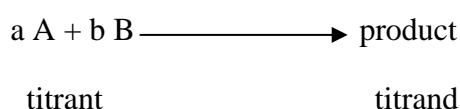**Part per million(ppm):** Milligrams of solute per liter of solution.

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

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

$$ppm = M \times M.wt \times 1000$$

For titrimetric reaction:

$$a\,A + b\,B \longrightarrow product$$

$$\underset{titrant}{\qquad} \qquad \underset{titrand}{\qquad}$$

titrant   titrand

At equivalent point:

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

$$N_A \times V_A = N_B \times v_B$$

or

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

Determination of the Molarity of an Acid or Base Solution

1. Select Type of Reaction
○ Strong Acid vs. Strong Base
◉ Weak Acid vs. Strong Base

2. Fill the Burette with
◉ Acid
○ Base

Total Volume of Acid [   ] ml

5. Push Slider Up to Add a Volume of Acid [   ] ml

Acid	Base
○ CH₃COOH	○ KOH
	○ NaOH
	○ Sr(OH)₂
	○ Ba(OH)₂

3. Select the Acid and Base

6. After Titration, Calculate and Enter Molarity of Acid [   ] M   OK

4. Select the Indicator
○ Methyl Red
○ Bromothymol Blue

Molarity of Base [   ] M   Volume of Base [   ] ml

Reset

Dropwise

Equivalent weights

(1) Equivalent weight in neutralization reactions.

The equivalent weight of acid is that weight of it which contains one-gram atom of replaceable hydrogen.

Ex: equivalent weight of H_2SO_4 = M.Wt H_2SO_4/2

equivalent weight of H_3PO_4 = M.Wt H_3PO_4/3

$$\text{eq.wt acid} = \frac{\text{M.Wt acid}}{\text{No. of active } H^+}$$

The equivalent weight of Base is that weight of it which contains one replaceable hydroxyl group.

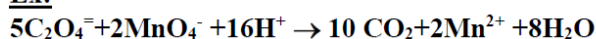**Ex: equivalent weight of NaOH = M.Wt NaOH/1**

$$\text{eq.wt base} = \frac{\text{M.Wt base}}{\text{No. of active } OH^-}$$

(2) Equivalent weight in Oxidation -reduction reactions.

The equivalent weight of an oxidant or a reductant is the number of electrons which 1moL of the substance gains or losses in the reaction.

$$\text{eq.wt} = \frac{\text{Formula weight (gm/mole)}}{\text{No. of lost or gained electrons}}$$

__Ex:__
$$5C_2O_4^= + 2MnO_4^- + 16H^+ \rightarrow 10\ CO_2 + 2Mn^{2+} + 8H_2O$$

$$\text{eq.wt } MnO_4^- = \frac{\text{F.wt } MnO_4^-}{5} \qquad\qquad \text{eq.wt } C_2O_4^= = \frac{\text{F.wt } C_2O_4^=}{2}$$

(3) Equivalent weight of complex formation and precipitation reactions.

Here the equivalent weight is the weight of the substance which contains or reacts with 1g. atm of a univalent cation M^+.

Ex: When silver nitrate reacts with sodium chloride, to form silver chloride, the equivalent weight of $AgNO_3$ is:

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3 \qquad\qquad \text{eq.wt } (AgNO_3) = \frac{\text{F.wt } AgNO_3}{1}$$
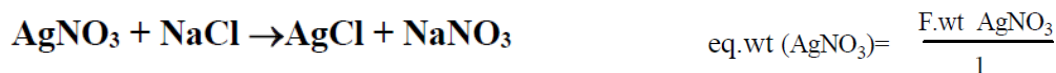
Experiment (5)

Calibration of Hydrochloric Acid

A- Preparation hydrochloric acid solution (0.1N):-

Taking a given volume of hydrochloric acid center by graduated cylinder (Graduated cylinder) and empties the bottle volumetric capacity (500 ML) and wash cylinder with distilled water and empties water washing in the bottle volumetric so as to make sure that all the acid been the center transfer to the bottle and then completes the volumetric size with distilled water to the mark in the volumetric bottle. calculate calibration hydrochloric acid status by the following equation.

1-Calculate the normality of the concentrated HCl :

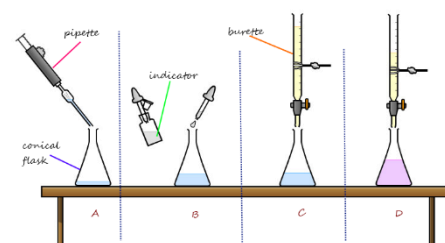$$N1= \frac{SP. * Wt.\% * 1000}{Eq.\ Wt.} \quad ------------ (1)$$

Where :-

N1 = hydrochloric acid calibratio n Centre

Sp. = Specific weight of acid (acid density)

Wt. % = The percentage of the weight of hydrochloric acid Center

$$N= \frac{1.19 * (37/100) *1000}{36.5} =12.0630$$

2- To prepare (500mL) of 0.1N HCl

Preparation titrated hydrochloric acid ($N_2 = 0.1$) and size ($V_2 = 500$ ML) Use the following formula to calculate the size of the acid Centre (V_1), which we take to prepare the acid diluted:

$$N_1 * V_1 = N_2 * V_2 \quad ----------(2)$$
$$\text{conc. HCl} \quad \text{dil. HCl}$$

$$V_1 = \frac{N_2 * V_2}{N_1} \quad -------- \quad (3)$$

$$12.0630 \times V_1 = 500 \times 0.1$$
$$V_1 = 4.1449\ mL$$

7

B: Preparation of (0.1N) sodium carbonate (Na₂CO₃):

The sodium carbonate solution is from standard solutions and is prepared by weighing a known amount of carbonate and dissolving in a known volume of distilled water. Where a bowl is weighed and it must be clean and dry in a delicate and accurate balance up to (0.1N) then a quantity of sodium carbonate is placed (that can be calculated) and weighed with a sensitive scale, then this amount is dissolved with a small amount of distilled water and then emptied into a volumetric flask and washed in a vessel several times With distilled water, wash water is added each time to the solution in the volumetric bottle, to ensure that all the carbonate material has transferred to the volumetric bottle, and then the volume is completed to the marker.

To calculate the weight of **sodium carbonate** needed to prepare a titration solution (0.1), the following equation is used:

$$N = \frac{Weight}{equivalent\ weight} * \frac{1000}{Volume(mL)}$$

$$Wt = \frac{N * V * Eq.Wt}{1000}$$

Where:
WT = weight of sodium carbonate dissolved in a volume of water
N = Standard of Sodium Carbonate to be prepared = 0.1
V = volume of the solution to be prepared (in ml)
Eq.Wt = equivalent weight to sodium carbonate

Equipment:-

1) burette of 50 ml.

2) 10 ml pipette.

3) 500ML Beaker.

4) 500 ML volumetric vial, 250 ML volumetric flask and conical flask.

5) funnel.

6) Spatule.

7) cylinder.

Procedure: -

A- Standardization of HCl solution with standard solution of Na_2CO_3

1-Clean the burette and rinse with HCl solution.

2-Fill the burette with HCl.

3-Pipet 10 ml of standard solution (Na_2CO_3) into a 250mL conical flask. Add 3 drops of **Methyl orange indicator**.

4-Titrate by adding HCl drop wise until the solution just beings to change from yellow to red.

5-Reapeat the titration a few times until you get approximate results. Take the average of the results and subtract 0.05mL. (This result represents the volume of extra drop which change the color of indicator.

6-Calculate the normality of HCl :

$$N_{acid} \times V_{acid} = N_{base} \times V_{base}$$

7-Make label on your bottle containing your name, date of preparation and concentration of acid after standardization.

8- The equation of reaction

$$Na_2CO_3 + HCl \xrightarrow{\text{M.O}} H_2CO_3 + 2NaCl$$
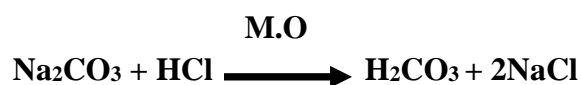
B- Analysis of sodium carbonate Na_2CO_3

1-Clean the burette and rinse with standardized HCl solution and then fill it with the acid.

2-Pipet 10 ml unknown solution (Na_2CO_3) into a 250mL conical flask. Add 2 drops of **phenolphthalein indicator** the solution will be pink.

3-Titrate by adding HCl drop wise until the solution just beings to change its color from pink to **colorless** this data will be (V_1).

4- Add 1-2 drops of **Methyl orange indicator** to the above solution which became yellow then complete the titration until the color of the solution became pale **orange (onion)**, this data will be (V_2).

5-Reapeat the titration a twice time until you gets approximate results. Take the average of the results and subtract 0.05mL. (This result represents the volume of extra drop which change the color of indicator.

6- Make a table as bellow: -

Sq		First titration	Second titration	Third titration	Average of titrations
1	Titration with ph.ph	V1	V1	V1	V1 (av.)
2	Titration with M.O	V2	V2	V2	V2 (av.)

$$V1(av.) = \frac{V1+V1+V1}{3}$$

$V1(av.) = 1/2 \ CO_3^=$

$V2(av.) = 1/2 \ CO_3^=$

$V1 + V2 = V_{tot.}$ of Na_2CO_3
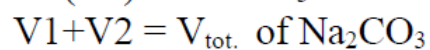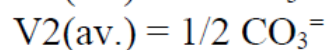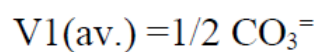
$$N_{acid} \times V_{(tot.) \ acid \ (from \ burette)} = N_{base} \times V_{base}$$

7- The equation of reaction :

$$Na_2CO_3 + HCl \xrightarrow{ph.ph} NaHCO_3 + NaCl$$
Pink   colorless

$$NaHCO_3 + HCl \xrightarrow{M.O} H_2CO_3 + NaCl$$
Yellow   pale orange

Buret

Volume is read before and after the titration

Solution of known concentration

Graduated markings

Stopcock

Known volume of substance being titrated

Wash bottle

Volume marker (calibration mark)

Weighed amount of solute

500 mL