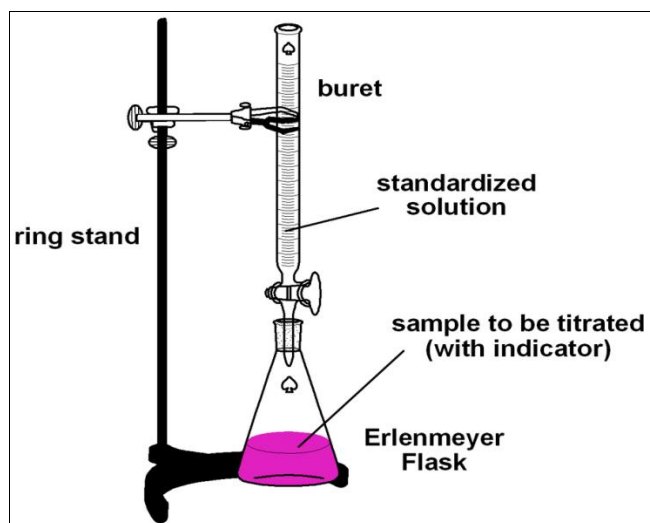# Alfarahidi University/ College of Pharmacy

Analytical Chemistry
1ˢᵗ class

Asst. lecturer
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Main Parts

Part 1 / Volumetric Measurement Glassware

Part 2 / Volumetric Calculations

Part 3 / Preparation of Solutions

Part 4/ Volumetric Analysis

List of Experiments

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General Personal Safety

1) Eating, drinking, smoking, applying cosmetics or lip balm, and handling contact lenses are prohibited in areas where specimens are handled.

2) Food and drink are not stored in refrigerators, freezers, cabinets, or on shelves, countertops, or bench tops where blood or other potentially infectious materials are stored or in other areas of possible contamination.

3) Long hair, ties, scarves, and earrings should be secured.

4) Appropriate Personal Protective Equipment (PPE) will be used where indicated:

- **Lab coats** or disposable aprons should be worn in the lab to protect you and your clothing from contamination. Lab coats should not be worn outside the laboratory.

- **Lab footwear** should consist of normal closed shoes to protect all areas of the foot from possible puncture from sharp objects and/or broken glass and from contamination from corrosive reagents and/or infectious materials.

- **Gloves** should be worn for handling blood and body fluid specimens, touching the mucous membranes or non-intact skin of patients, touching items or surfaces soiled with blood or body fluid, and for performing venipunctures and other vascular access procedures. Cuts and abrasions should be kept bandaged in addition to wearing gloves when handling biohazardous materials.

- **Protective eyewear** and/or masks may need to be worn when contact with hazardous aerosols; caustic chemicals and/or reagents are anticipated. Eye goggles should be worn:

a. When working with certain caustic reagents and/or solvents, or concentrated acids and bases.

b. When performing procedures that are likely to generate droplets/aerosols of blood or other body fluid.

c. When working with reagents under pressure.

d. When working in close proximity to ultra-violet radiation (light).

5) NEVER MOUTH PIPETTE! Mechanical pipetting devices must be used for pipetting all liquids.

6) Frequent hand washing is an important safety precaution, which should be practiced after contact with patients and laboratory specimens. Proper hand washing techniques include soap, running water and 10-15 seconds of friction or scrubbing action. Hands should be dried and the paper towel used to turn the faucets off.

- **Hands are washed:**
a. After completion of work and before leaving the laboratory.
b. After removing gloves.
c. Before eating, drinking, smoking, applying cosmetics, changing contact lenses or using lavatory facilities.
d. Before all other activities which entail hand contact with mucous membranes or breaks in the skin.
e. Immediately after accidental skin contact with blood or other potentially infectious materials.
f. Between patient contact and before invasive procedures.

7) Laboratory work surfaces must be disinfected daily and after a spill of blood or body fluid with a 1:10 dilution of Clorox in water.

- Wearing contact lenses in the laboratory is discouraged and requires extra precaution if worn. Gases and vapors can be concentrated under the lenses and cause permanent eye damage. Furthermore, in the event of a chemical splash into an eye, it is often nearly impossible to remove the contact lens to irrigate the eye because of involuntary spasm of the eyelid. Persons who must wear contact lenses should inform their supervisor to determine which procedures would require wearing no-vent goggles.

The Analytical Chemistry

Analytical chemistry is branch of chemistry science deal with identification and separation of compounds and mixture, then determination of the proportions of the constituents. Analytical chemistry mainly deals with:

   A. Qualitative analysis.

   B. Quantitative analysis.

A - Qualitative analysis (Identification):

Provides information about the identity of species or functional groups in the sample (an analyte can be identified).

B - Quantitative analyses:

Provides numerical information of analyte (quantitate the exact amount or concentration) that it is important to know the level of drug in blood or urine.

- ## Methods of analysis:

A- Classical methods

   1. Gravimetric Methods

   2. Volumetric Methods

B- Instrumental methods

   1. Spectroscopic Methods

   2. Chromatographic Methods

   3. Electroanalytical Methods

PART 1
### Volumetric Measurement Glassware

1- **Burette:** A piece of glassware used for carefully measured volume of a liquid regent come in various sizes, consists of calibrated tube figure (1). Containing the liquid a value arrangement by which flow from a tip can be controlled.

> **Note:** The precision attainable with a burette is better than with measuring pipet.

Figure (1): Burette

2- **Pipet:** A piece of glassware used for measuring the volume of Liquid comes in various sizes. All pipets are designed for transfer of known volumes of Liquids from one container to another, there were two types of the pipets:

A. Volumetric or transfer pipet: Have one calibration mark and are used for deliver a single specific volumes or fixed volumes of Liquids quite accurately, figure (2a).

B. The other kind of pipette, the Mohr pipette, has graduations that permit a range of volumes to be dispensed very easily, but somewhat less accurately (figure 2b).
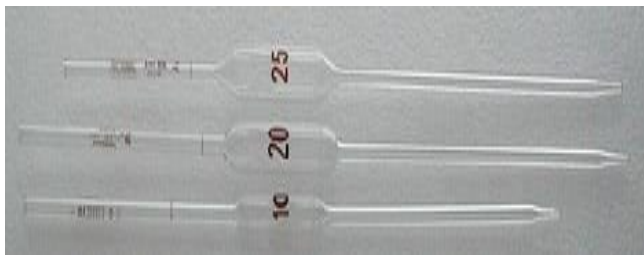

(a)   (b)

Figure (2): (a) volumetric pipette, (b) mohr pipette

• **Cleaning of Pipettes:**

Not only can a dirty pipette contaminate your sample, it can also dispense the wrong volume. Liquid sticks to the walls of a dirty pipette, so one test for a clean pipette is to check that the solution does not bead on the walls as it is dispensed. Unless you are being provided a new pipette by the technician, it is a good idea to wash your pipette as outlined in the following steps:

1. Place a small volume of the solution to be pipetted into a beaker.
2. Draw the solution into the pipette using a propipette (figure 3a) or pipette pump (figure 3b) and then tilt and turn the pipette until all of the inner surfaces have been wetted by the solution.
3. Discard this washing solution as waste.
4. Repeat the previous steps again until beading is not observed on the inner walls of the pipette.
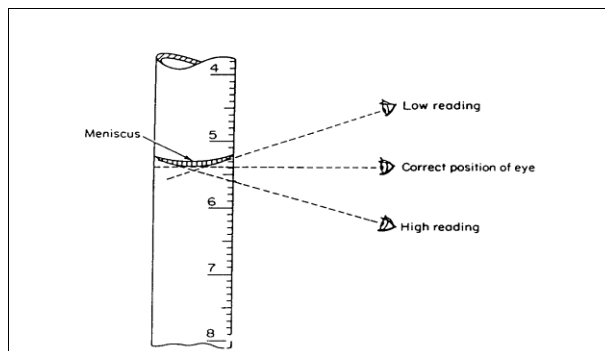
(a)　　　　　　　　　　　**(b)**
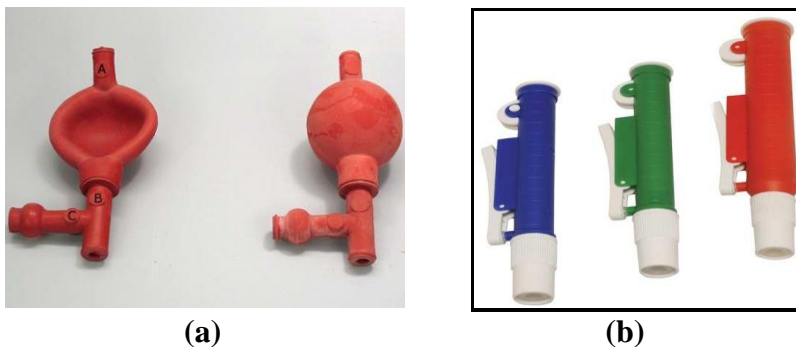
Figure (3): (a) propipette, (b) pipette pump

3- Graduated cylinder: A piece of glassware used for handling measured approximate volume of Liquids.

Figure (4): Cylinders

> **Note:** Volumetric glassware should be read with your eyes at the level of the meniscus, in order to avoid parallax errors.

Figure (5): Technique for reading a meniscus

4- Volumetric flask: A peace of glassware manufactured with a flat bottomed bulb with an elongated neck calibrated to hold a set volume at a mark on the neck. The flask may also be called a graduated flask or measuring flask because its mark specifies a precise volume measurement. capacities ranging from 5 mL to 5 liters It is used to make up a solution to a known volume. Volumetric flasks measure volumes much more precisely than beakers or Erlenmeyer flasks.

Figure (6): Volumetric flask

5- Conical flask (Erlenmeyer flask): A peace of glassware come in various sizes. Conical flasks are designed so that the liquid contents can be swirled or stirred without spilling. The neck reduces the loss of evaporating contents . It is named after the German chemist Richard Erlenmeyer created it in 1860. It is using for:
a. Titration
b. Filtration
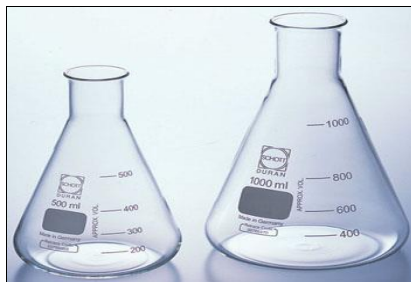
c. Distillation

d. Heating and evaporation

Figure (7): Erlenmeyer flask

6- **Funnel:** A funnel is a pipe with a wide mouth that helps to pour substances into a container without spilling. In a chemistry lab, funnels are often used together with filters to separate a mixture.


Figure (8): Funnel

7- **The beaker:** A piece of glassware come in various sizes, used for:
   a- Dissolving the samples
   b- Transfer the solution
   c- Container of solution (TC)

Figure (9): Beaker

8- Stirring glass rod: A peace of glassware come in various sizes used for:
a. Mixing chemicals and liquids.
b. Helps to direct liquid poured out of a beaker, flasks, etc., so it doesn't run down the side of the vessel.
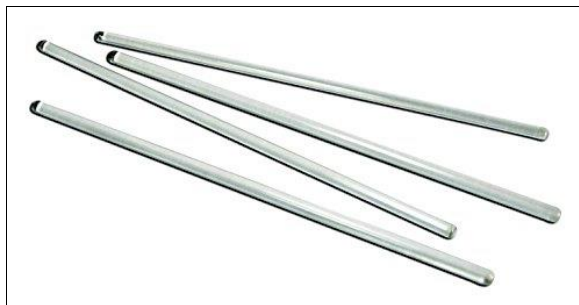
Figure (10): Stirring glass rod

8- Watch glass: is a circular concave piece of glass used in chemistry as a surface to evaporate a liquid, to hold solids while being weighed, for heating a small amount of substance and as a cover for a beaker.

Figure (11): Watch glass

9- Spatula: A piece of laboratory tools used for transferring the solid material from a reagent bottle without contamination, manufactured from steel or plastics.

Figure (12): Spatula

10- Polyethylene wash bottle: A piece of laboratory tool used for washing the glassware, manufactured from polyethylene flexible. Wash bottles may be filled with a range of common laboratory solvents and reagent, according to the work to be undertaken. These include deionized water, detergent solutions, and rinse solvents such as acetone, isopropanol, or ethanol. In biological labs, it is common to keep sodium hydrochloride solution in a wash bottle to disinfect unneeded cultures.

11- Brush: A piece of laboratory tool used for cleaning the glassware comes in a various sizes.

Figure (13): Spatula

12- Sensitive Electronic Balance: Analytical balance can weigh up to 200 g of substance in $10^{-4} – 10^{-5}$ g precision.

Figure (14): Sensitive Balance

13- Clamp (Burette clamp): equipment which consists of a metal pole with a solid, firm base, used to hold, or clamp, laboratory glassware.
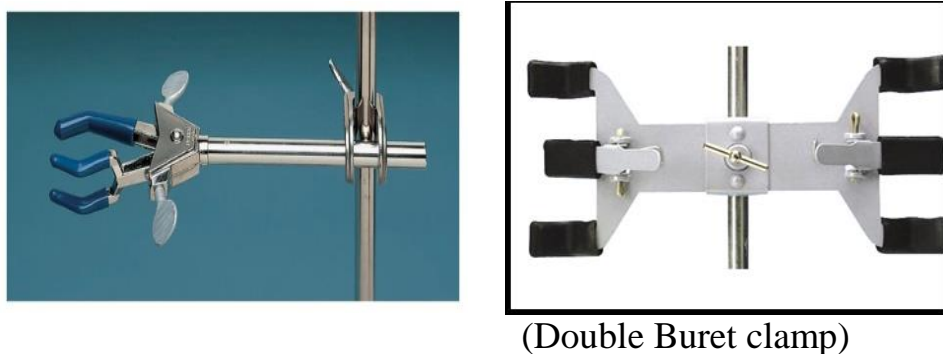

(Double Buret clamp)

Figure (15): Clamp

14- Boss Head: (Clamp holder): Used for attaching clamps and other equipment to the rod.

Figure (16): Boss Head

15- Stand: A piece of laboratory tools used to hold the burette attached to a clamp during titration.

Figure (17): stand

Laboratory Techniques

- **Handing Chemicals**

1- Solids:

Solid chemicals are usually stored in wide-mouth bottles. Always check the label carefully before removing any chemical. Remove the lid or stopper, place the lid or stopper so that it will not be contaminated, tilt the bottle and roil it gently back until the desired amount of the solid fails into the bottle lid. Do not waste material. If a solid reagent is compacted or "caked" ask your instructor for assistance. Chemical should never be returned to the bottle from which they were removed-discard any excess.
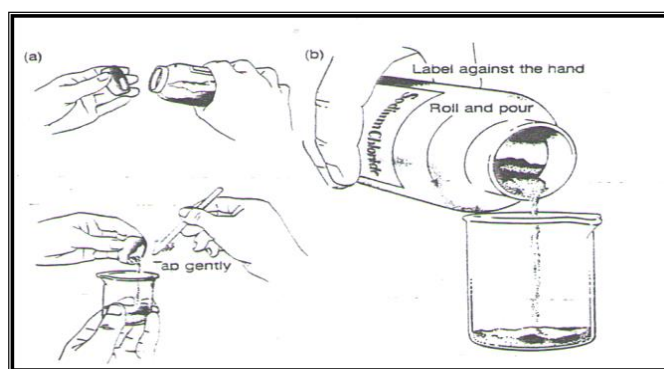

Figure (18): Transfer of solid from a reagent bottle

2- Liquids:

Many commonly used laboratory reagents are solutions while others are (pure) liquids such as alcohol or acetone. Liquid reagents are stored in a variety of bottles such as those shown in Figure (2).
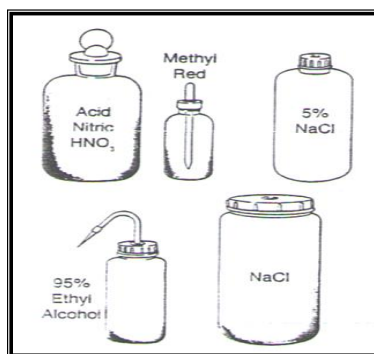

Figure (19): Common reagent bottles for liquids and solids

Squeeze dropper bottles or bottles fitted with eye droppers are used when very small amounts of the liquids are required in experiments. When larger amounts of liquid are required standard reagent bottles are often used. Hazardous reagents are stored in special bottles with self-fitting dispensers (Brinkman Dispensettes, Akso SMI) Figure 3 illustrates the transfer of a liquid from a standard reagent bottle. You should always check the label on reagent bottle carefully before you remove any liquid from the bottle. Careful checking of labels prevents many unnecessary accidents.
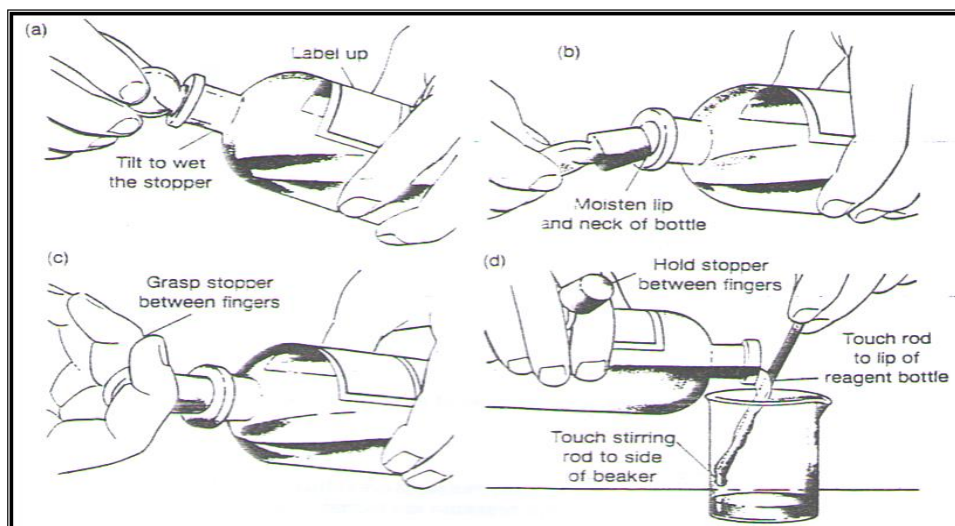

Figure (20): Transferring liquid from a reagent bottle

- **Volumetric glassware handling**

1. Using of Graduate Cylinders:

Graduate cylinders are used to measure approximate volumes of liquid. Hold the graduated cylinder vertical at eye level and look at the top surface (meniscus) of the liquid. The meniscus is curved (concave) with a fairly flat section in the center. By nothing the position of this flat section relative to the calibrated marks you can estimate the volume of a liquid to within approximately 0.2mL with a 25mL graduated cylinder.
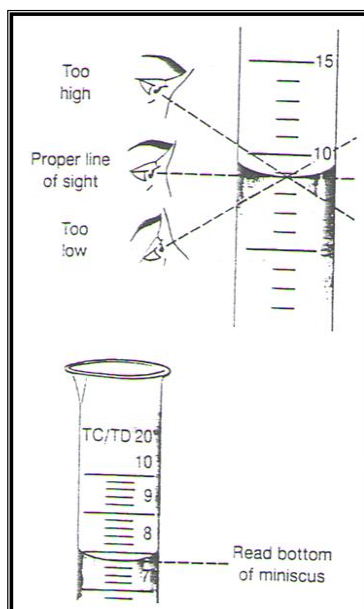
Figure (21): Proper technique for reading a burette or a graduated cylinder

2. Using of Volumetric Pipets:

Always use a pipet bulb or aspirator to fill pipets. Volumetric pipets have one calibration mark and are used to deliver specific volumes of liquids quite accurately. The pipets is rinsed with distilled water and then with small portions of the liquid to be measured. A small amount of the liquid is drawn into the pipet. The pipet is held nearly horizontal and rolled so that the liquid comes in contact with the interior surface of the pipet. Finally the liquid is allowed to drain through the tip. After the pipet has been rinsed with the liquid three times, liquid is drawn into the pipet until the liquid level stands above the calibration mark. The tip of the pipet is then wiped with a clean towel, the liquid is allowed to fall to the mark, and the hanging drop is removed by touching the tip of the pipet against the wall of the waste beaker. The specified amount of liquid is then allowed to drain into a new beaker. When the liquid appears to have drained from the pipet, wait 20 seconds, touch the tip of the pipet to the (inside) surface of the container to remove the hanging drop and remove the pipet. Do not blow out the last bit of liquid in the pipette. When the above instructions are followed the pipet will deliver the specified volume. Pipets are available in a variety of sizes commonly, 5, 10, 25 and 50 mL. Figure 2 illustrates the use of volumetric pipets.
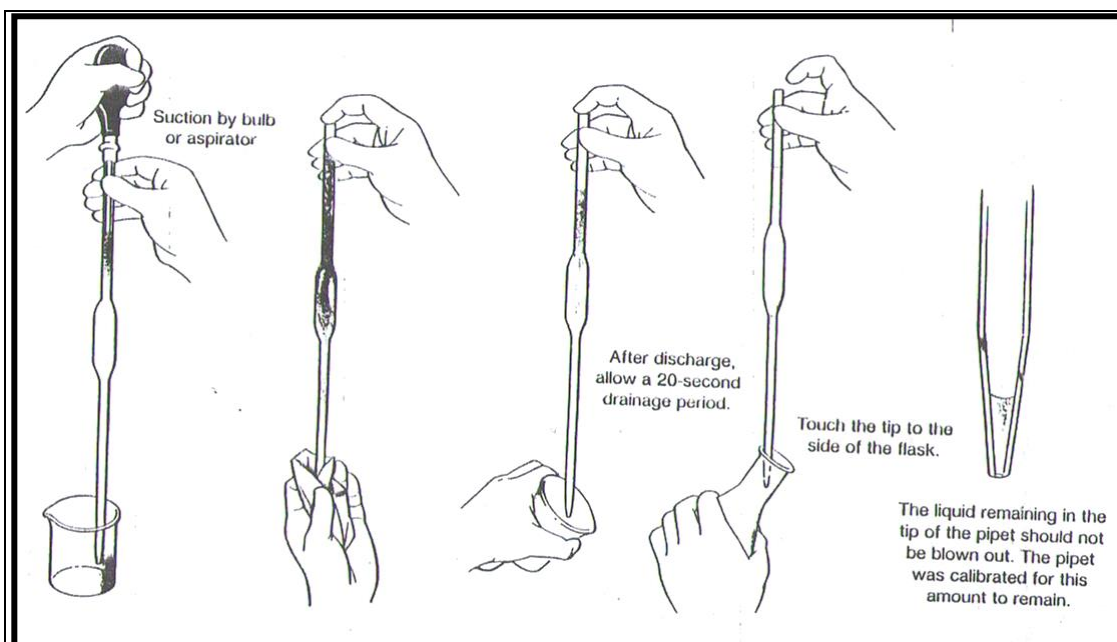
Figure (22): Use of a volumetric pipet

A measuring pipet (Mohr pipet) is graduates along its length and is used to deliver various volume of liquid.

3. Burettes and Titration Procedures:

Burets are used to measure the volume of a liquid reagent required to reach with a carefully measured (liquid or solid) sample of another substance. Burets are washed with detergent solutions. If water droplets adhere to the inner wall of a burette, use a burette brush and detergent solution to wash it. The end of the buret brush must not touch the stopcock because stopcock grease will spread over the inner wall of the burette. Teflon stopcocks do not require grease. Exercise caution to prevent the wire handle of the burette brush from scratching wall of the buret. No water droplets adhere to the inner walls of a clean buret.

Check the stopcock in the clean burette. If the stopcock is ground glass it should be stopcock grease in the hole (or in the buret) and there should be no "dry streaks" on the stopcock. If there is a problem, return the stockroom and obtain another. Stockroom personnel with organic solvents will be used to clean stopcock.

> **CAUTION**: The organic solvent is flammable. Its vapors are poisonous – avoid inhaling them.

Apply a very small amount of grease near both ends of the stopcock, insert into the barrel, and rotate gently until both surfaces are covered with a thin film of stopcock grease.

Burets are calibrated from TOP TO BOTTOM. Fifty mL burets are calibrated in 0.1 mL increments and thus it is possible to estimate volumes to within 0.01 mL.

A clean buret is rinsed with distilled water and then three times with approximately 5 mL portions of the liquid to be measured. Hold the buret nearly horizontally and rotate it so that the liquid comes in contact with all the interior surface. The rinse liquid is then allowed to drain through the tip. The buret is then filled with liquid above the calibration mark. Excess liquid is allowed to drain through the tip until no air bubbles remain and the tip is filled with liquid. The volume of the liquid in the calibrated part of the buret is then read and recorded. It is not necessary to begin with a reading of 0.00 mL, since the volume of the titrant is calculated by difference of final and initial volumes. Liquid is dispensed from the buret until the desired reaction is complete. The buret is read again. The initial reading is subtracted from the final reading to obtain the volume of liquid.

The sample to be titrated is usually placed in an Erienmeyer flask (the receiving flask). The stopcock is used to control the rate at which the liquid in the buret, the titrant, is added to the receiving flask (Figure 3). The receiving flask is rotated gently during the titration to ensure through mixing. A piece of white paper should be placed under the receiving flask so that the indicator color change can be detected easily. Near the endpoint of the titration (the color fades slowly) the inner wall of the receiving flask should be "washed down" with distilled water so that all of the titrant comes into contact with the solution being titrated.
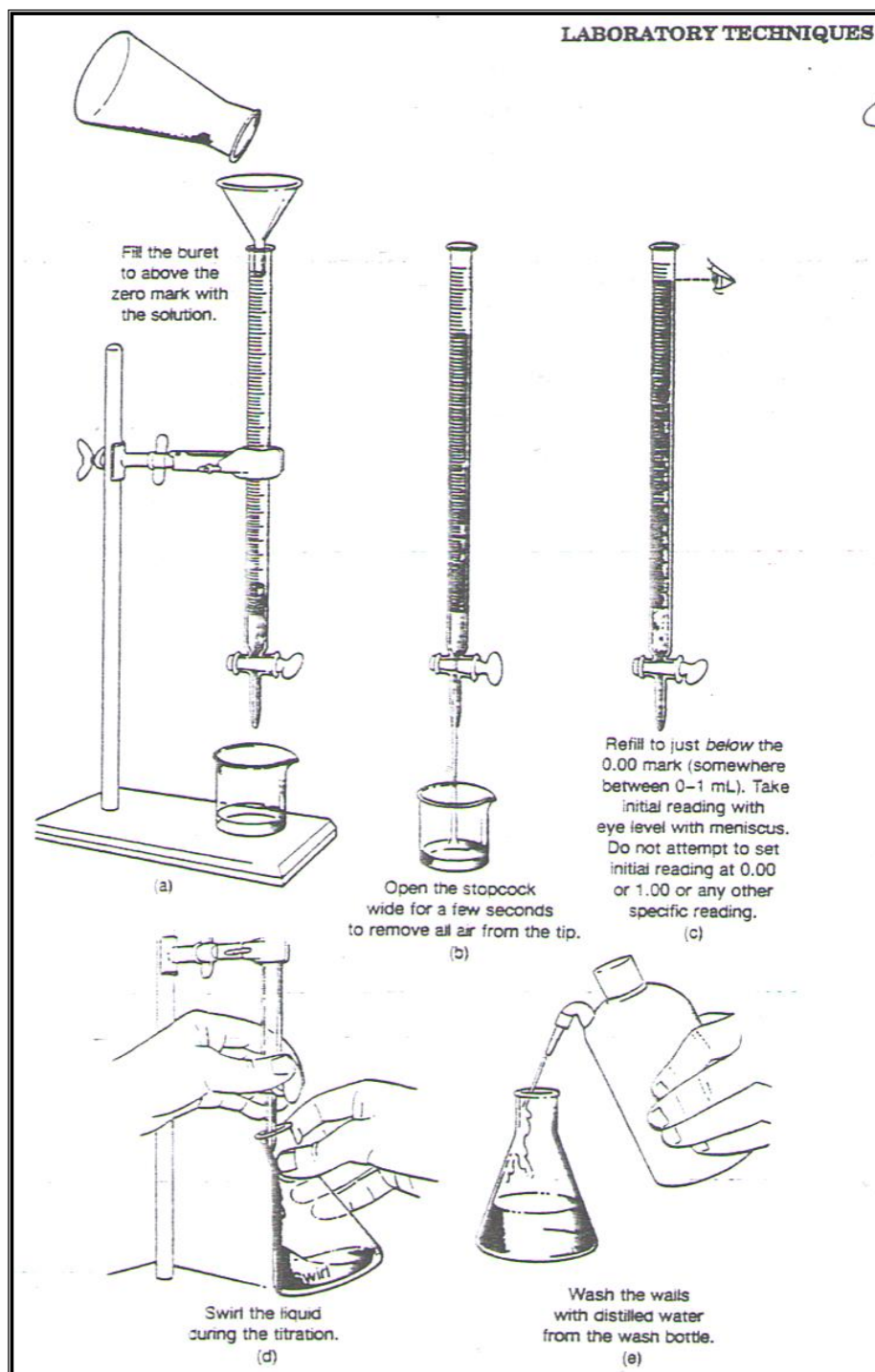
Figure (23): Techniques of titration (a) Filling a buret (b) Operation of stopcock (c) Adding titrant (d) Swirling liquid (e) Washing wall of receiving flask

4. Volumetric Flasks:

Volumetric flasks are constructed to contain (not deliver) the volume specified on the flask. They are available in many sizes. Figure 4 shows a volumetric flask and includes directions for its use.
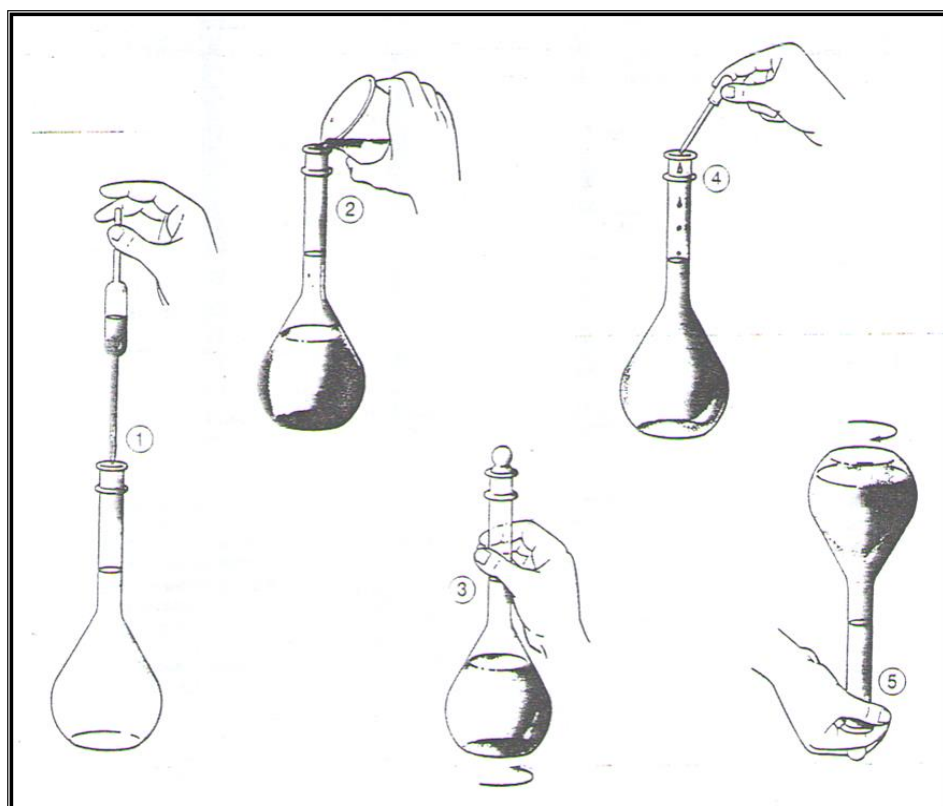
Figure (24): Use of a volumetric flask. (1) Place measured amount of solute in flask (2) Fill flask (with distilled water) to 80% of volume (3) Stopper and shake until solute dissolves (4) Carefully fill to calibration line with distilled water (5) Invert flask at least 10 times to measure complete mixing

PART 2

Volumetric Calculations

- **Some Important Units of Measurement**
- **SI Units (International System of Units (SI)**

In this system the units of mass, length, time, temperature, and the amount of substance are measured in kilograms, meters seconds, Kelvin, and moles respectively. Mass is a measure of the amount of matter in an object. Weight is the pull of gravity. It varies with location.

The mole (abbreviated mole) is the SI unit for amount of a chemical specie, it is always associated with a chemical formula and represents Avogadro's number (6.022 X 10) of particles represented by that formula.

The molar mass (μ) of a substance is the mass in grams of 1mol of that substance. Molar masses are calculated by summing the atomic masses of all the atoms appearing in a chemical formula.

$$\text{Mole} = \frac{\text{Wight of the sample (g)}}{\text{Molar mass (g/mole)}}$$

Example: How many moles of Fe are in 5.6 g Fe? How many Fe atoms are contained in the sample?

- **Expressing concentration of solution**

We express the concentration of solutions in several ways. For standard solutions used in titrimetry, either molarity C or normality N is usually employed. The first term gives the number of moles of reagent contained in one liter of solution, and the second gives the number of equivalents of reagent in the same volume.

1. **Molarity:** is the number of moles of solute dissolved in one liter of solution. The units, therefore are moles per liter, specifically it is moles of solute per liter of solution.

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Liter of solution}}$$

$$\text{Molarity} = \frac{\text{Weight (g)}}{\text{Molecular Weight (g/mol)}} \times \frac{1000}{\text{Volume (mL)}}$$

Molecular Weight = Sum. Of atomic weight

Example: What is the molarity of a 5.00 liter solution that was made with 10.0 moles of KBr?

Solution: We can use the original formula. Note that in this particular example, where the number of moles of solute is given, the identity of the solute (KBr) has nothing to do with solving the problem.

$$\text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Liters of solution}}$$

Given: no. of moles of solute = 10.0 moles
Liters of solution = 5.00 liters

$$\text{Molarity} = \frac{10.0 \text{ moles of KBr}}{5.00 \text{ Liters of solution}} = 2.00 \text{ M}$$

Example: Prepare 0.1 M of NaCl in 250 mL of D.Water from Solid

Solution: Wt. = M x M.wt. x V (mL) / 1000
                 $= 0.1 \times 55.5 \times 250 / 1000 = 1.38$ g

2. **Normality:** is the number of equivalents of solute dissolved in one liter of solution. The units, therefore are equivalents per liter, specifically it is equivalents of solute per liter of solution.

$$\text{Normality} = \frac{\text{No. of equivalents of solute}}{\text{liter of solution}}$$

$$\text{No. of equivalents} = \frac{\text{Weight (g)}}{\text{Equivalent Weight (g/eq)}}$$

$$\text{Normality} = \frac{\text{Weight (g)}}{\text{Equivalent weight (g/eq)}} \times \frac{1000}{\text{Volume (mL)}}$$

$$\text{Eq.W t} = \frac{\text{M.Wt}}{n}$$

- For acids; n = No. of (H) atoms, for HCl n=1
- For bases; n = No. of (OH) groups, for NaOH n=1
- For salts; n = No. of Cation (M^+) or anion atoms (M^-), for Na_2CO_3 n= 2
- For oxidants and reductants; n = No. of gained or lost electrons, for $KMnO_4$ n= 5
- **Relationship between Molarity and Normality**

$$\text{Molarity} = \frac{\text{Weight (g)}}{\text{Molecular Weight (g/mol)}} \times \frac{1000}{\text{Volume (mL)}}$$

$$\text{Normality} = \frac{\text{Weight(g)}}{\text{Equivalent weight (g/eq)}} \times \frac{1000}{\text{Volume (mL)}}$$

$$\text{Eq.Wt} = \frac{\text{M.Wt}}{n}$$

▸ At constant volume $\longrightarrow \mathbf{N = M \times n}$

3. **Molality (m)**: Tells us the number of moles of solute dissolved in exactly one kilogram of solvent (represented by a lower case m).

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{mass of solvent in Kg}}$$

Example: If you have 10.0 grams of Br_2 and dissolve it in 1.00 L of cyclohexane, what is the molality of the solution? The density of cyclohexane is 0.779 kg/L at room temperature .

Solution:
First, work out the number of moles of bromine. Br_2 has a molecular weight of 159.8 g/mole, so we have
 10g / (159.8 g/mole) = 0.063 moles Br_2
Next, convert the volume of solvent to the weight of solvent using the density
1.0L × 0.779 kg/L = 0.779 kg
Now just divide the two to get the molality
0.063 moles Br_2/ 0.779 kg cyclohexane = 0.080 m

4. Percent concentration

Concentrations expressed in terms of percent (parts per hundred). Percent composition of a solution can be expressed in several ways. Three common methods are:

- Weight – Volume Percent (% W/V)

$$\% W/V = \frac{\text{Weight of solute (g)}}{\text{Volume of solution (mL)}} \times 100$$

- Weight – Weight Percent (% W/W)

$$\% W/W = \frac{\text{Weight of solute (g)}}{\text{Weight of solution (g)}} \times 100$$

- Volume – Volume Percent (% V/V)

$$\% V/V = \frac{\text{Volume of solute (mL)}}{\text{Volume of solution (mL)}} \times 100$$

Example: What is the weight/volume percentage concentration of 250mL of aqueous sodium chloride solution containing 5g NaCl?
Solution:
Calculate the weight/volume (%) = mass solute ÷ volume of solution x 100
mass solute (NaCl) = 5g
volume of solution = 250mL
(w/v%) = 5g ÷ 250mL x 100 = 2g/100mL (%)

Example: 2.0L of an aqueous solution of potassium chloride contains 45.0g of KCl, what is the weight/volume percentage concentration of this solution in g/100mL ؟
Solution:
a. Convert the units (mass in grams, volume in mL):
    mass KCl = 45.0g
    volume of solution = 2.0L = 2.0 x 1000mL = 2000mL

b. Calculate w/v (%) = mass solute (g) ÷ volume solution (mL) x 100
    w/v (%) = 45.0 ÷ 2000mL x 100 = 2.25g/100mL (%)

5. **Parts per Millions (ppm)**

$$C\ ppm = \frac{Weight\ of\ solute\ (mg)}{Volume\ of\ solution\ (L)}$$

$$C\ ppm = \frac{mass\ solute\ (g)}{Volume\ of\ solution\ (mL)} \times 1000\ 000$$

- **Relationship between PPM and Molarity and Normality**

$$C\ ppm = M\ x\ M.wt\ x\ 1000$$

$$C\ ppm = N\ x\ Eq.wt\ x\ 1000$$

Example: 150mL of an aqueous sodium chloride solution contains 0.0045g NaCl .
Solution:
Calculate the concentration of NaCl in parts per million (ppm) .
a. ppm = mass solute (mg) ÷ volume solution (L)
b. mass NaCl = 0.0045g = 0.0045 x 1000mg = 4.5mg
Volume solution = 150mL = 150 ÷ 1000 = 0.150L
Concentration of NaCl = 4.5mg ÷ 0.150L = 30mg/L = 30ppm

Example: What mass in milligrams of potassium nitrate is present in 0.25kg of a 500ppm KNO_3 (aq.)?
Solution:
a. ppm = mass solute (mg) ÷ mass solution (kg)
b. Re-arrange this equation to find the mass of solute :
mass solute (mg) = ppm x mass solution (kg)
c. Substitute in the values :
mass KNO_3 = 500ppm x 0.25kg = 125mg

PART 3

Preparation of Solutions

A Solution is a homogenous mixture of two or more substances. There are three types of solutions:

• **Saturated solution** is a solution containing the maximum amount of solute that will dissolve at a given temperature.

• **Unsaturated solution** is a solution in which more solute can be dissolved at a given temperature.

• **Supersaturated solution** is a solution that contains more solute than would dissolve in a saturated solution at a given temperature.

Solutions have a wide variety of uses in the pharmaceutical industry. They are used therapeutically as vehicles for oral, parenteral, topical, otics, ophthalmic, and nasal products. They are also used as flavorings, buffers, preservatives, and suspending agents for a variety of liquid dosage forms.

Aqueous solution is a type of solution, where water is the solvent. Aqueous solutions are the most prevalent of the oral solutions, in which drugs are dissolved in water along with any necessary flavorings, preservatives, or buffering salts.

Water acts as universal solvent that almost all substances are soluble in water in. Substances are classified into two types, depending upon the affinity towards water; hydrophilic substance Substances, which are soluble in water (Hydrophilic means, "water loving" substances includes acids, bases, and many salts, and hydrophobic substances, substances which does not dissolve in water include many organic molecules, including fats and oils.

Solubility is the capacity of solute to dissolve in a pure solvent also it can defined as the number of milliliters of solvent in which 1 gm of solute will dissolve.

• **Factors affecting solubility:** depends upon the physical and chemical properties of the solute and the solvent. Several factors can affect the solubility of a solute such as,

1. Temperature

2. pH

3. Particle size

4. Crystal structure

5. Molecular structure

6. Pressure

7. Nature of solvent (non-polar, polar protic, or polar aprotic solvents)

Electrolytes is a substance which form ions when dissolved in water or certain other solvents (completely ionizes) and thus produce solutions that conduct electricity. Strong electrolytes ionize essentially completely in a solvent, whereas weak electrolytes ionize only partially.

Table 1: Examples of strong and weak electrolytes

Strong	Weak
Inorganic acids such as HNO_3, $HCIO_4$, H_2SO_4, HCl, HI, HBr, $HClO_3$, $HBrO_3$	Many inorganic acids, including: H_2CO_3, H_3BO_3, H_3PO_4, H_2S, H_2SO_3
Hydroxides Alkali and alkaline-earth	Most organic acids
Most salts	Ammonia and most organic bases
	Halides, cyanides, and thiocyanates of Hg, Zn, and Cd
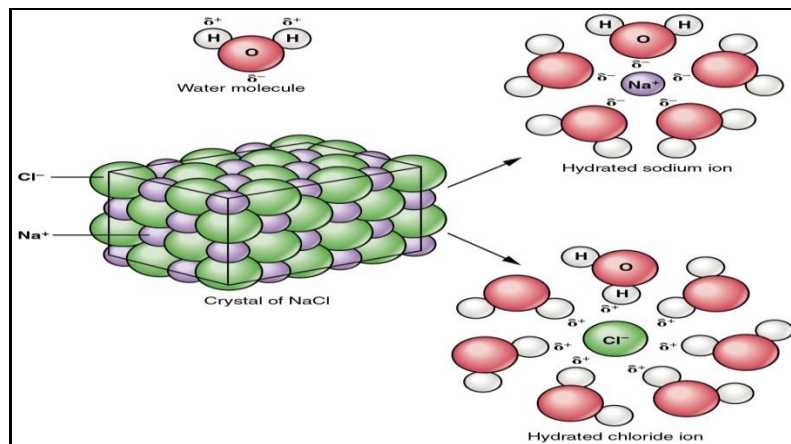
Figure 25: solvent property of water

- **Types of Solubility:**
1. Solubility of solids in liquids
2. Solubility of liquids in liquids
3. Solubility of gases in liquids

1. Solubility of solids in liquids

Experiment 1

- ## Preparation of (0.1N) Na_2CO_3 in 250 mL

- **Chemicals and equipment:**
1- Na_2CO_3
2- Beaker
3- Distilled water as a solvent
4- Glass rode
5- Washing bottle
6- Volumetric flask (250mL)

- **Procedure**:
- Calculate the weight of (**Na_2CO_3**) you need to prepare (0.1 M) in (250 mL).
- M.wt of $Na_2CO_3 = 23×2 + 12 + 16×3 = 106$

$$N = \frac{wt}{eq.wt} \times \frac{1000}{V(ml)}$$

1. N = 0.1
2. V = 250 mL
3. Eq. wt = 53
4. Wt = ( )

$$0.1 = \frac{wt}{53} \times \frac{1000}{250} \gg wt = 1.325 gm$$

- Weigh (1.325gm) of Na_2CO_3, Dissolve and complete the volume in volumetric flask with (250 mL) by using distilled water.

Example: Prepare 1% NaCl Solution from solid NaCl.
Solution:
1% means 1gm of NaCl dissolved in 100mL of distilled water, then;

Wt. = 1gm   V = 100 mL
M.wt of NaCl = (1x23) + (1x35.5) = 58.5 gm/mol

$$M = \frac{Wt\ (mg)}{M.wt\ (mg/mol)} \ X\ \frac{1000}{Volume}$$

$$M = \frac{1\ gm}{58.5\ gm/mol} \ X\ \frac{1000}{100} \longrightarrow M = 0.17\ M$$

2. Solubility of liquids in liquids

- **The Dilution**

We can define dilution as a procedure used to prepare a solution with a less concentration from a more concentrated solution. Stock solutions are stronger solutions that you can later dilute to the desired strength ordered. The larger volume that you mix with the stock solution is called the diluent. You can use the following formula to calculate dilutions:

Moles of solute before dilution = Moles of solute after dilution

$$C_1V_1 = C_2V_2$$

C = Concentration mole / L
V = Volume L
Note that/ V_2 always larger than V_1, and always lesser than C_1 ($C_2 < C_1$).

- Concentration of solute before dilution

$$Normality = \frac{Specific\ Gravity\ (g/l)\ x\ Percentage\ (\%)\ x\ 1000}{Equivalent\ Weight\ (g\ /eq)}$$

$$Molarity = \frac{Specific\ Gravity\ (g/l)\ x\ Percentage\ (\%)\ x\ 1000}{Molecular\ Weight\ (g/\ mol)}$$

The specific gravity of a substance is the ratio of its mass to the mass of an equal volume of water at 4°C.

Example: Describe the preparation of 900 mL of 3.00 M HNO_3 from the commercial reagent that is 70.5% HNO_3 (w/w) and has a specific gravity of 1.42.
Solution:

$$Molarity = \frac{Specific\ Gravity\ (g/l)\ x\ Percentage\ (\%)\ x\ 1000}{Molecular\ Weight\ (g/\ mol)}$$

$$M\ HNO_3 = \frac{1.42 \times (70.5/100) \times 1000}{63} = 15.9$$

$$M_1\ V_1 = M_2\ V_2 \longrightarrow 15.9\ x\ V1 = 3\ x\ 900$$

$$V1 = 159\ mL \quad diluted\ to\ 900\ mL$$

Experiment 2

A. Preparation of (0.1N) HCl in (250 mL) from concentrated HCl

CAUTION: **HCl (Hydrochloric Acid) is a corrosive acid,** handle with care. **If you spill any on your skin or clothing, wash immediately with water. Measure the volume of concentrated HCl by using graduated cylinder and add acid to water.**

- **Chemicals and equipment**
1- Concentrated HCl
2- Distilled water as a solvent
3- Graduated cylinder
4- Funnel
5- Washing bottle
6- Volumetric flask of (250mL)

- **Procedure:**
- Concentrated HCl has specific gravity of (1.185) and (38%). The normality of the concentrated reagent is:

$$N = \frac{sp.\,gr \times 1000 \times \%}{M.wt}$$

$$N = \frac{1.185 \times 1000 \times 38/100}{36.5} = 12\ N$$

- Calculate the volume of concentrated HCL that should be taken to prepare 250 mL of (0.1N) HCl

Conc. HCL   =   diluted HCL
 $N_1\ V_1$ = $N_2\ V_2$
12   $\times V_1 =$ 0.1×250 $\longrightarrow$ $V_1 = 2.2$ mL

 - We will work with following steps:
1- Transfer distilled water to a volumetric by using washing bottle (~20 mL).
2- Measuring volume (2.2 mL) of 0.1N, HCl by using graduated cylinder.
3- Transfer this (2.2 mL) of acid to the volumetric flask (250 mL).
4- Complete the volume to the calibration ring by adding the solvent (distilled water).
5- Slop the volumetric flask, and shake well.

B. Preparation of (0.10N) HCl and dilute solutions of (0.010N), (0.020N) and (0.030N) of HCl

In this experiment, we have concentrated solution of HCl, we will dilute **(0.10N)** of HCl to **(0.010 N)**, **(0.020N)**, **(0.030N)**.

- **Chemicals and equipment**
1- HCl (0.10N)
2- distilled water as a solvent
3- Beaker
4- Graduated cylinder
5- Washing bottle
6- Volumetric flask

- **Procedure:**
- We want to dilute (0.10N) of flask with 100.0 mL, according to the following equation:

$$N_1 V_1 = N_2 V_2$$

$$0.10 \times V_1 = 0.010 \times 100mL \longrightarrow V_1 = (\ ) mL$$

- We will work with following steps:
1- Transfer distilled water to a volumetric flask (100 mL) by using washing bottle (20 mL of DW).
2- Measuring volume of 0.1 N HCl by using graduated cylinder.
3- Transfer this of acid to the volumetric flask (100 mL).
4- Complete the volume to the calibration ring by adding the solvent (distilled water).
5- Slop the volumetric flask, and shake well.

PART 4

Volumetric Analysis

Volumetric analysis is a widely-used quantitative analytical method. As the name implies, this method involves the measurement of volume of a solution of known concentration which is used to determine the concentration of the analyte. The titration is one of the most common volumetric analysis techniques used to measure the concentration of chemical substance in a certain solution. The most common way of carrying out this procedure is to put the unknown solution (the analyte) in an Erlenmeyer flask and then, using a burette, slowly add the titrant (standard solution) to it. The procedure is based on the reaction between the titrant and the analyte, then measuring the volume of a standard solution of an appropriate reagent whose precise concentration is already known.

The equivalence point is the point in a titration when the amount of added standard reagent is exactly equivalent to the amount of analyte.

The end point is the point in a titration when a physical change occurs that is associated with the condition of chemical equivalence.
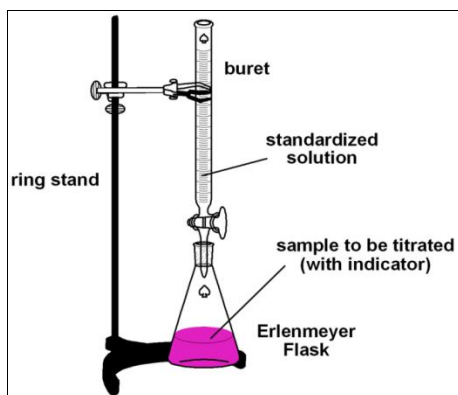
Figure (25): Titration apparatus

- **Types of Titrations**:

There are many types of titrations with different procedures and goals.
  - ❖ Acid – Base titration (neutralization titration)
  - ❖ Redox titration
  - ❖ Complexometric titration
  - ❖ Precipitation Titrations
  - ❖ Gas phase titration
  - ❖ Karl Fischer titration (Potentiometric)

A. Neutralization Titration (Acid-Base titration)

Acid-base titrations depend on the neutralization between an acid and a base when mixed in solution. The reaction is characterized by a rapid change in pH near the equivalence point, a change that is readily detected by an acid-base indicator or that can be followed electrically by use of a pH meter.There are three types of Neutralization Titration:

1. Strong acid and strong base

2. Weak acid and strong base

3. Weak base and strong acid

Neutralization titrations are performed with standard solutions of strong acids or strong bases. The accuracy of a volumetric method is closely related with the accuracy of the concentration of the used in the titration. A primary standard is the standard solution that serves as a reference material in all titrimetric methods, most commonly Na_2CO_3, $H_2C_2O_4$, $HClO_4$, H_2SO_4, and KOH. The important requirements for a primary standard are:

- Has known concentration
- Stability in air
- High purity
- Atmospheric stability
- Independent of humidity
- Modest cost
- Large molar mass

A few volumetric reagents are obtainable in such a high state of purity that they can be used for the direct preparation of standard solutions. Many others, including some of the most useful, cannot be so used, either because they are hydrated like NaOH or because for some other reason as HCl that is volatile liquid they cannot be guaranteed to have the degree of purity necessary. A reagent of this kind (a secondary standard) is standardized against a pure compound (a primary standard).

pH Indicators are often added to the analyte solution to produce an observable physical change (the end point) at or near the equivalence point. The indicators most commonly used in neutralization titrations are highly colored organic compounds which have the property of changing color when the hydrogen ion concentration of the solution is changed over a certain range.
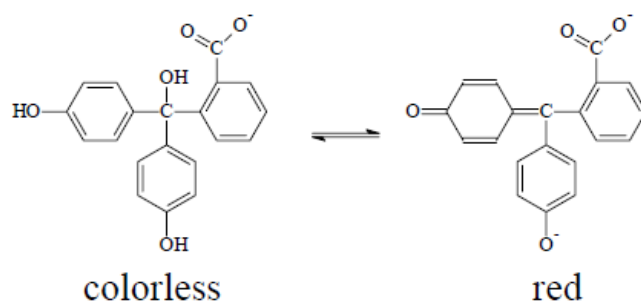
colorless   red

Figure (27): Color change for phenolphthalein

Table2: The Common Acid/Base Indicators

Indicator	Color change interval (pH)	Acid	Base
thymol blue	1.2 - 2.8	red	yellow
methyl orange	3.1 - 4.4	orang	yellow
methyl red	4.4 - 6.2	red	yellow
chlorophenol red	5.4 - 6.8	yellow	Red
bromothymol blue	6.2 -7.6	yellow	Blue
phenol red	6.4 - 8.0	yellow	Red
thymol blue	8.0 - 9.6	yellow	Blue
Phenolphthalein	8.0 - 10.0	colorless	Magenta
alizarin yellow	10.0 -12.0	yellow	green

Experiment 3

Preparation of approximately of (0.1N) HCl and standardization it with (0.1N) Na$_2$CO$_3$

Standardization is a process of determining the concentration of a substance in solution by adding a standard reagent of known concentration to it in carefully measured amounts until a reaction of definite and known proportion is completed and then calculating the unknown concentration.
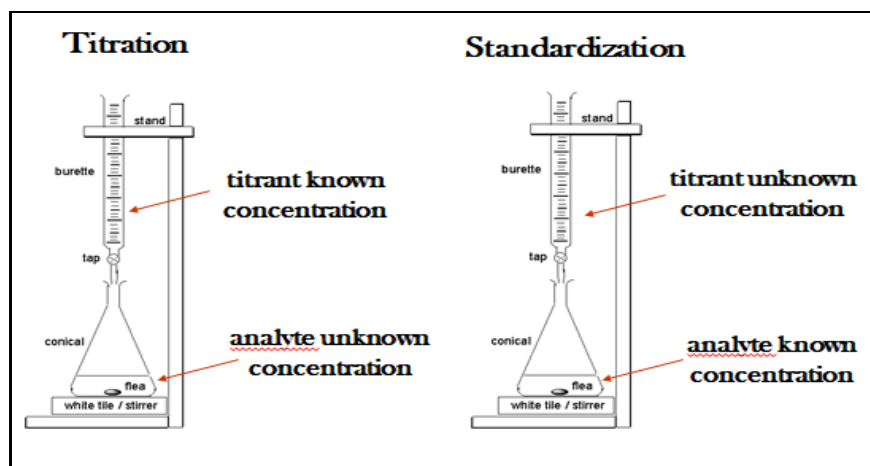
Figure (26): Neutralization titration

Standardized the HCl is most commonly employed in volumetric analysis. Concentrated HCl with (12N-10.5N) contains approximate (35%) from hydrochloride with specific gravity of (1.185). We will standardize the ~0.1 N HCl solution (the titrant) with sodium carbonate (Na$_2$CO$_3$) using methyl orang as the indicator. Na$_2$CO$_3$ is a base and reacts with the strong acid HCl in the following way:

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

- ## Procedure

A. Preparation of 0.1N of Na_2Co_3

- Calculate the weight of (Na_2CO_3) you need to prepare (0.l N) in (250 mL).
- Weigh (2.65gm) of Na_2CO_3, Dissolve and complete the volume in volumetric flask with (250 mL) by using distilled water.

B. Preparation (0.1N) of HCl in (250 mL) from concentrated HCl:

We will work with following steps:
1. Transfer distilled water to a volumetric by using washing bottle (20 mL of DW).
2. Measuring volume (2.2 mL) of 0.1N, HCl by using graduated cylinder.
3. Transfer this (2.2 mL) of acid to the volumetric flask (250 mL).
4. Complete the volume to the calibration ring by adding the solvent (distilled water).
5. Slop the volumetric flask, and shake well.

C. Standardization of prepared 0.1N HCl

1. Fill burette with the prepared HCl solution
2. Transfer (10 mL) of exactly (0.1N) Na2CO3 solution (primary standard) to a conical flask.
3. Add 2 drops of methyl orange as an indicator, yellow color is obtained.
4. Place a white sheet of paper under the flask to aid in the detection of any color change.
5. Titrate with HCl drop by drop from the burette into the conical flask until a faint orang color was obtained.
6. Repeated the titration up to three times then calculated the average of V of HCl. For accurate work, the differences between the reading should not exceed 0.1 mL.
7. The exact normality of HCL can be calculated from the following equation :
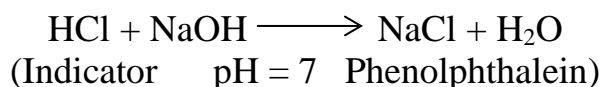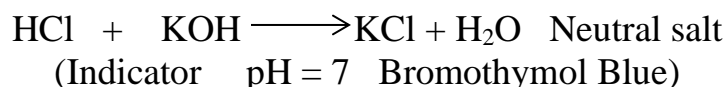
$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

$$N_1 \ V_1 \text{ of } Na_2CO_3 \quad = \quad N_2 \ V_2 \text{ of HCl}$$

Titration of Strong Acids and Strong Bases

Strong acids are completely dissociated in solution; therefore, the number of moles (equivalents) of base (OH^-) required neutralizing the acid equals the number of moles (equivalents) of acid (H^+) present. The equivalence point is the end of a titration where the stoichiometry of the reaction is exactly satisfied, or:

$$moles\ H^+ = moles\ OH^-$$

$$HCl\ +\ KOH \longrightarrow KCl + H_2O \quad Neutral\ salt$$
$$(Indicator \quad pH = 7 \quad Bromothymol\ Blue)$$

$$HCl + NaOH \longrightarrow NaCl + H_2O$$
$$(Indicator \quad pH = 7 \quad Phenolphthalein)$$

If we start plotting the pH of the analyte against the volume of NaOH that we are adding from the burette, we will get a titration curve as shown below.
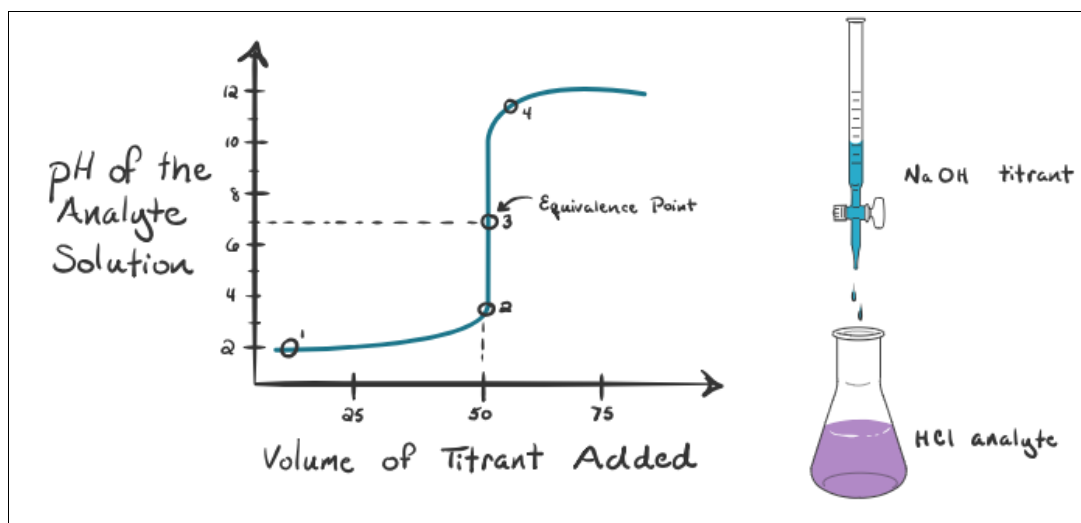

Figure (28): Acid-Base titration curve

Experiment 4

Preparation and Standardization of 0.10 N NaOH

- **Procedure**

A. Preparation of an (0.1N) NaOH

a. $N = \dfrac{WT}{eq.wt} \times \dfrac{1000}{VmL}$

        1. $N = 0.1$
        2. $V = 250$ mL
        3. Eq. wt $= 40$
        4. $Wt = X =$

b. Weigh (1gm) of NaOH, dissolve it and dilute in volumetric flask with (250 mL) by using distilled water.

B. Standardization of (0.1N) NaOH solution

1- Transfer (10 mL) of standard HCl solution to conical flask.

2- Add (1-2) drops of phenolphthalein (ph. ph.) as indicator it will be colorless.

3- Place a white sheet of paper under the flask to aid in the detection of any color change.

4- Fill burette with the prepared NaOH solution.

5- Start titration by adding NaOH drop by drop into the conical flask until the color of the solution is faint pink.

6- Repeated the titration up to three times then calculated the average of V of HCl. For accurate work, the differences between the reading should not exceed 0.1 mL.

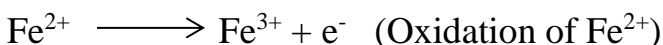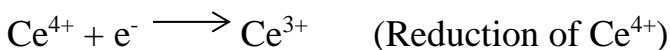7- The exact normality of NaOH is obtained from the following equation :

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

$$N_1 V_1 = N_2 V_2$$

$$\text{(NaOH)} \qquad \text{(HCl)}$$

B. Oxidation–Reduction Titration

Oxidation-reduction reactions (redox reactions) are reactions in which electrons are transferred from one reactant to another reactant. **Oxidation** is defined as the loss of electrons and **reduction** as the gain of electrons. Oxidation–Reduction is among the most important reactions in chemistry, biochemistry, and industry.

$$Ce^{4+} + e^- \longrightarrow Ce^{3+} \quad \text{(Reduction of } Ce^{4+})$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad \text{(Oxidation of } Fe^{2+})$$

Originally, the term ((Oxidation)) referred, not only to reactions with oxygen; it now is used to describe any process in which the oxidation number of a species increases, even if oxygen is not involved in the reaction.

Redox titration is based on the redox reaction (oxidation-reduction) between analyte and titrant. A reducing agent is an electron donor while an oxidizing agent is an electron acceptor.

- **Common Oxidants agents and Reductants agents:**

Oxidizing agents: $KMnO_4$, Cerric ammonium sulphate, Ceric ammonium nitrate, KIO_3, $KBrO_3$, $K_2Cr_2O_7$, etc.

Reducing agents: Oxalic acid, $SnCl_2$ (Stannous chloride), As_2O_3, Mohr salt (Ferrous ammonium sulphate $(NH_4)_2FeSO_4.6H_2O$), $Na_2S_2O_3$ (Sodium thiosulphate) etc.

Example: Which of the following is a redox reaction?
(a) $Cl_2 + 2NaBr \longrightarrow Br_2 + 2NaCl$

(b) $BaCl_2 + K_2SO_4 \longrightarrow BaSO_4 + 2KCl$
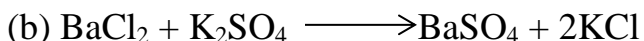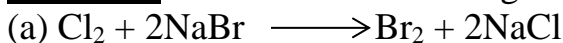
The following substances can be used as primary standard; Mohr's salt, Iodine, Sodium oxalate ($Na_2C_2O_4$), $K_2Cr_2O_7$, KIO_3, $KBrO_3$, and As_2O_3, all of which could be obtained in pure state. Their standard solution can be prepared by direct method i.e. by dissolving a known amount of the dried substance in water and then making up to a known volume in a measuring flask.

Experiment 5

Preparation and Standardization of 0.10N KMNO₄ Solution against Oxalate

CAUTION: H_2SO_4 (Sulfuric Acid) is A corrosive oxidizing Acid be careful when handling with it. If it drops on your skin or clothing, wash immediately with water. If you get any in your eyes, wash your eyes gently with lots of water and get your instructor's help immediately.

Solution of permanganate ion is strong oxidizing reagent. Its half-reaction is:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
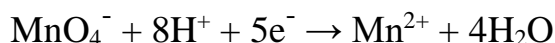
Aqueous solutions of permanganate are not entirely stable which decompose slowly because of water oxidation and thus it requires occasional restandardization:

$$4MnO^{4-} + 2H_2O \rightarrow 4MnO_2 + 3O_2 + 4OH^-$$

Because the decomposition reaction is slow, it is catalyzed by light, heat, acids, bases, manganese(II), and manganese dioxide, thus standardized permanganate solutions should be stored in the dark. Removal of manganese dioxide by filtration before standardization markedly improves the stability of standard permanganate solutions. The color of permanganate solutions is intense enough to serve as an indicator in titrations. The permanganate end point is not permanent because excess permanganate ions react slowly with the relatively large concentration of manganese(II) ions present at the end point, according to the reaction:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 2MnO_2 + 4H^+$$

$KMnO_4$ solution can be standardized by following three methods:
(i)   By using sodium oxalate or oxalic acid
(ii) By using As_2O_3
(iii) By using Mohr's salt as primary standard

Of all the above methods, oxalic acid is most trustworthy since it can be obtained in 99.9% purity method. A standard solution of the oxalate ion in acidic solutions, is converted to the undissociated acid. Thus, its reaction with permanganate can be described by

$$2KMnO_4 + 4H_2SO_4 + 5C_2H_2O_4 \rightarrow 2KHSO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

- **Procedure**

I. Preparation of 0.1 N KMnO₄ solution

1. Dissolve (0.8 gm) of solid $KMnO_4$ in (250 mL) distilled water by using Beaker and stirring rod.
2. Heat the solution on hotplate for about one hour at 70-80 C.
3. Filter the solution by using glass wool funnel then store the solution in the dark bottle.

II. Prepare of (0.1N) H₂C₂O₄ Oxalic acid solution

a. $N = \dfrac{WT}{eq.wt} \times \dfrac{1000}{VmL}$

   1. N = 0.1

                                             2. V = 250 mL

                                             3. Eq. wt = 45

                                             4. Wt = X =

b. Weigh (1.125gm) of $H_2C_2O_4$, dissolve it and dilute in volumetric flask with (250 mL) by using distilled water.

III. Standardization of (0.1N) NaOH solution

1- Fill the burette with previously prepared $KMnO_4$ solution.
2- Transfer 10mL of (0.1N) oxalic acid to a conical flask and add 10mL of concentrated H_2SO_4.
3- Shake to homogenize the solution homogeneous.
4- Add few drops of $KMnO_4$ then heat the solution to about (60-90) ˚C until a pink color is disappeared.
5- Titrate with potassium permanganate solution running in from a burette with constant stirring, do it very slowly at the beginning of the titration, waiting for color to disappear after the addition of each drop.
6- Titrate to a pink color that persists for about 30 seconds which was the end point.
7- Repeated the titration up to three times then calculated the average V of $KMnO_4$. For accurate work, the differences between the readings should not exceed 0.1 ml.
8- The exact normality of $KMnO_4$ is obtained from the following equation:

$$N_1 V_1 \; = \; N_2 V_2$$

$$(KMnO_4) \qquad (H_2C_2O_4)$$
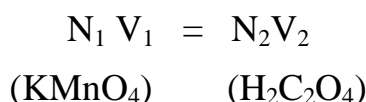
Experiment 6

Determination of Iron In Crystallized Ferrous Sulphate By Potassium Permanganate

In this experiment, the percentage of iron in an unknown iron oxide sample is determined by titration with a standard solution of potassium permanganate. The overall reaction is:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$
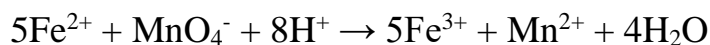
- **Procedure**
1- Transfer by pipette 10mL of unknown concentration of Iron sulfate to a conical flask then add 10mL concentrated H_2SO_4 (2N).
2- Shake to homogenize the solution homogeneous.
3- Titrate with standardized potassium permanganate solution running in from a burette with constant stirring.
4- Titrate to a pink color that persists for about 30 seconds which was the end point.
5- The exact normality of $KMnO_4$ is obtained from the following equation :

$$N_1 V_1 \; = \; N_2 V_2$$

$$(KMnO_4) \qquad (FeSO_4)$$

C. Complexometric Titrations

Complexation reactions have many uses in analytical chemistry, but their classical application is in **complexometric titrations.** Titrimetric methods based on complex formation, have been used for more than a century.

The technique involves the titrating of metal ions with complexing agent, which is commonly known as the ligands as a matter of fact that most metal ions react with electron-pair donors (ligand) to form coordination compounds or complexes. A ligand is an ion or neutral species that forms a covalent bond with a cation or a neutral metal atom by donating a pair of electrons, which are then shared by the two (ligand, must have at least one pair of unshared electrons available for bond formation). These may be simple ions such as Cl^-, small molecules such as H_2O or NH_3, larger molecules such as $H_2NCH_2CH_2NH_2$ (ethylenediamine) or even very large macromolecules, like proteins etc.

Most often, in complexometric titrations the ligand is the titrant and the metal ion the analyte in which a metal ion reacts with a suitable ligand to form a complex, and an indicator or an appropriate instrumental method determines the equivalence point.

EDTA forms chelates with practically most of the metal ions and this fact is exploited in the complexometric determination of these ions using EDTA. Such titrations are called **complexometric** or **chilometric** or **EDTA titrations.**

Ethylenediaminetetraacetic acid-also called (ethylenedinitrilo) tetraacetic acid which is commonly shortened to EDTA, is the most widely used complexometric titrant. EDTA has the structural formula:
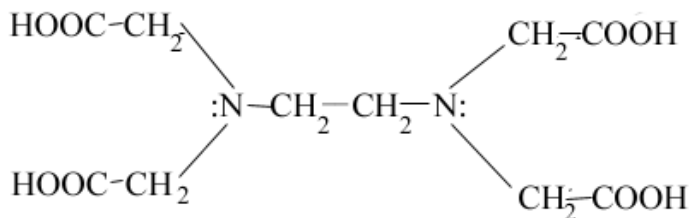

Figure (29): Structure of EDTA

The EDTA molecule has six potential sites for bonding a metal ion: the four carboxyl groups and the two amino groups, each of the latter with an unshared pair of electrons. Thus, EDTA is a hexadentate ligand.
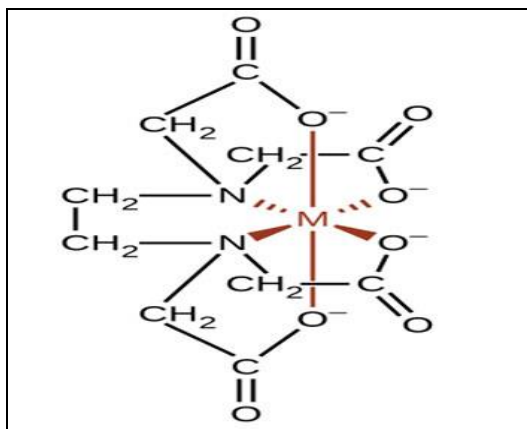
Figure (30): M-EDTA complex structure

     Metallochromic indicators or metal ion indicators are the compounds that are capable of forming a complex with the metal ion being determined. In favorable conditions, the metal-indicator complex formed has an intense color, which is distinctly different from the uncomplexed indicator. At present, several different indicators are available for each metal ion.

Indicator	Useful pH range	Useful for
Calmagite	9 – 11	Ba, Ca, Mg, Zn
Eriochrome Balck T	7.5-10.5	Ba, Ca, Mg, Zn
Eriochrome Blue R	8-12	Ca, Mg, Zn, Cu
Murexide	6-13	Ca, Ni, Cu
PAN	2-11	Cd, Cu, Zn
Salicylic acid	2-3	Fe

Experiment 7

Determination of Calcium and Magnesium ions concentration in a sample of water (determination of water hardness)

Water that has not been purified is what is known as hard water. Water hardness is an expression for the sum of the calcium Ca^{2+} and magnesium Mg^{2+} cation concentration in a water sample. These cations form insoluble salts with a reagent in soap, decreasing its cleaning effectiveness. The standard way to express water hardness is in mg/L (ppm) $CaCO_3$ and $MgCO_3$.

An excellent way to determine water hardness is to perform a complexometric titration using a standard ethylenediaminetetraacetic acid (EDTA) solution. Due to steric hindrances, EDTA will complex with calcium and magnesium in a 1:1 molar ratio. A blue dye called Eriochrome Black T (ErioT) is used as the indicator. This blue dye also forms a complex with the calcium and magnesium ions, changing colour from blue to wine-red in the process.

The dye–metal ion complex is less stable than the EDTA–metal ion complex so that the indicator is added return blue as all the Ca^{2+} and Mg^{2+} ions present are complexed with the EDTA. For the titration, the sample solution containing the calcium and magnesium ions is reacted with an excess of EDTA.
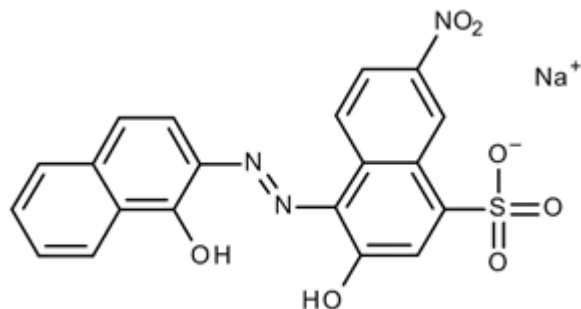

Figure (31): Eriochrome black –T structure

I. Preparation of 0.01 M EDTA solution
1- Weigh out about 4.0 g of disodium dihydrogen EDTA dehydrate.
2- Dissolve the solids in water and transfer this solution into a clean 500 mL volumetric flask.
3- Dilute with water to the line. If the solution is turbid, add a few drops of 0.1 M sodium hydroxide. Mix solution thoroughly.

II. Standardisation of the EDTA Solution
1- Pipet 10 mL portions of the standard magnesium sulfate solution into 250 mL Erlenmeyer flasks.
2- Add 2 mL portions to each flask of the ammonia-ammonium buffer and 5 drops of Erichrome Black T indicator.
3- Full the burette with prepared EDTA solution.
4- Titrate EDTA to the point where the color changes from wine-red to pure blue. Do not stop titrating at a violet or purple color.
5- Repeated the titration up to three times then calculated the average of the volume of EDTA used to titrate.
6- The exact normality of EDTA is obtained from the following equation:

$$M_{MgSO4} \, V_{MgSO4} \; = \; M_{EDTA} V_{EDTA}$$

III. Titration Method for Tap Water Samples
1- Pipet 10 mL portions of water sample into 250 mL Erlenmeyer flasks.
2- Add 2 mL portions to each flask of the ammonia-ammonium buffer and 5 drops of Erichrome Black T indicator, a wine-red solution will be resulted from the formation of Mg^{2+}-indicator complex and Ca^{2+}-indicator complex.
3- Titrate this solution with standardized EDTA to the point where the color changes to pure blue.
4- Repeated the titration up to three times then calculated the average of the volume of EDTA used to titrate.
5- The total weight of both Mg^{2+} and Ca^{2+} is obtained from the following equation:

$$M_{EDTA} V_{EDTA} = 1000 \text{ wt. Mg+Ca (gm)}/ (24+40 \text{gm/mol})$$

$$\text{Wt. \% (Mg+Ca)} = (M \times V)_{EDTA} \times (24+40)/100$$

D. Precipitation Titrations

Precipitation titrimetry, which is based on reactions that yield ionic compounds of limited solubility, is one of the oldest analytical techniques, dating back to the mid-1800s. Because of the slow rate of formation of most precipitates, however, there are only a few precipitating agents that can be used in titrimetry. By far the most widely used and most important precipitating reagent is silver nitrate, which is used for the determination of the halides, the halide-like anions (SCN^-, CN^-, CNO^-), mercaptans CH_3SH, fatty acids, and several divalent and trivalent inorganic anions.

$$Ag^+ + I^- \longrightarrow AgI \text{ (precipitate)}$$

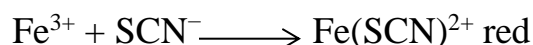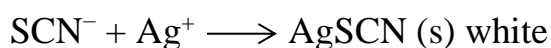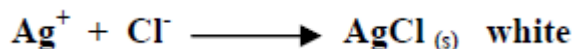$$KI + AgNO_3 \longrightarrow AgI + KNO_3 \downarrow$$
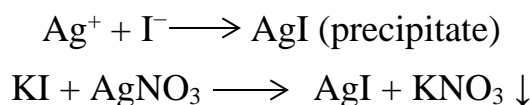
The end point produced by a chemical indicator usually consists of a color change or, occasionally, the appearance or disappearance of turbidity in the solution being titrated. The color change should take place with change in the titration curve.

Based on the indicator used in the determination of the end point the precipitation titrations are classified into three types. They are as follows:

Mohr's method: In this method potassium chromate solution is used as the indicator. This method is used in the determination of the Cl^-, Br^- and CN^- by using silver nitrate as the titrant in neutral or slightly acidic condition. The end point is detected by the formation a brick-red silver chromate (Ag_2CrO_4) precipitate in the equivalence-point region.

$$Ag^+ + Cl^- \longrightarrow AgCl_{(s)} \quad \text{white}$$

$$2Ag^+ + CrO_4^{-2} \longrightarrow Ag_2CrO_{4\,(s)} \quad \text{red}$$
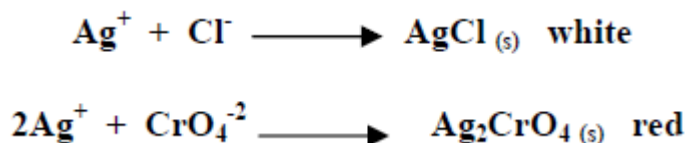
Volhard's method: In this method ferric ion is used as the indicator. This method is also known as the indirect method. The most important application of the Volhard method is the indirect determination of halide ions. A measured excess of standard silver nitrate solution is added to the sample containing chloride ion, and the excess silver is determined by back-titration with a standard thiocyanate solution (SCN^-). Once all the silver ions have reacted, the slightest excess of thiocyanate reacts with Fe^{3+} to form a dark red complex.

$$Ag^+ + Cl^- \longrightarrow AgCl_{(s)} \text{ white}$$

$$SCN^- + Ag^+ \longrightarrow AgSCN \text{ (s) white}$$

$$Fe^{3+} + SCN^- \longrightarrow Fe(SCN)^{2+} \text{ red}$$

Fajan's method: Fluorescein is used as the indicator that is useful for the titration of chloride ion with silver nitrate. The mechanism involved is that the indicator is adsorbed to the surface of the precipitate and shows the color change as reddish. The adsorption occurs near the equivalence point and results not only in a color change but also in a transfer of color from the solution to the solid. In aqueous solution, fluorescein partially dissociates into hydronium ions and negatively charged yellow-green fluoresceinate ion. The fluoresceinate ion forms an intensely red silver salt.

Fluorescein   Fluoresceinate anion
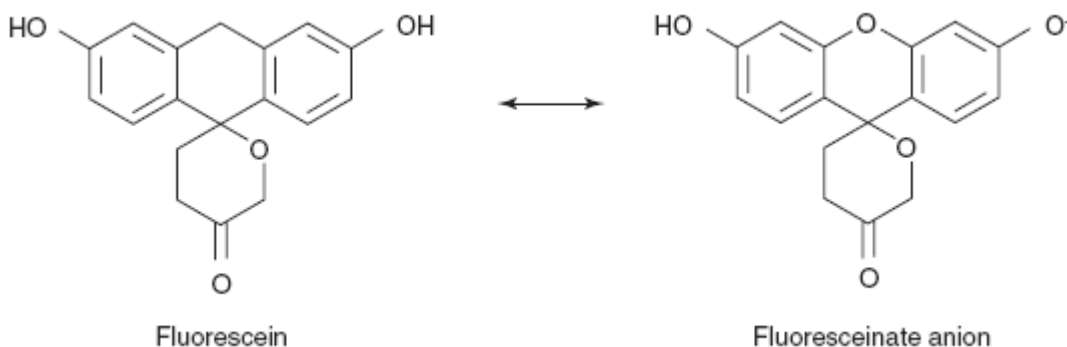
- **Factors affecting the precipitation titrations**
    1. Nature of the solvent
    2. pH of the solution
    3. Concentration of the reactants
    4. Low solubility product formation during the titration
    5. The nature and concentration of the foreign substances
    6. Temperature is directly proportional to the precipitation formation
    7. Order of addition of the reagents

Experiment 8

Determination of Chloride Ion by the Mohr Method

The Mohr method was first described in 1865 by a German pharmaceutical chemist (K. F. Mohr), who was a pioneer in the development of titrimetry. The principle of Mohr's method depends on the fractional precipitation of silver chloride and silver chromate. Since the former is considerably less soluble, silver chromate does not precipitate until the solution is free from chloride ion. At the end point the chromate ions combine with silver ions to form the sparingly soluble red silver chromate.

- **Procedure**
    1. Transfer (10 mL) of the unknown solution containing Cl^- ion into a conical flask
    2. Add few drops of K_2CrO_4, which used as an indicator.
    3. Titrate with standard (0.05 N) silver nitrate solution slowly until a faint reddish precipitate appeared is stable.
    4. Repeat the titration and calculated the average of volume then deduct the volume of silver nitrate that reacts with the indicator.

- **Calculation**

The percent of Cl^- ion in the sample is calculated in 10 mL of as shown below

$N_1V_1 = N_2V_2$

0.1 N $AgNO_3$ = 1000 wt. Cl (gm)/35.5(gm/mol)

Cl % = (N x V) $AgNO_3$ x 0.035 x 100/ 10 %

Final V= V of $AgNO_3$ consumed for the titration of sample - V of $AgNO_3$ consumed for the titration of blank.