The University
of Al-Mustansiriyah

College of
Pharmacy

Dep. of
pharmaceutical
chemistry

Practical
analytical
chemistry

Text for

first class

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CONTENTS

عزيزي الطالب :-

من أجل سلامتك وسلامة الجميع وللمحافظة على المختبر ومحتوياته , يجب قراءة ما يلي وبشكل جيد والعمل وفق ما فيها من ارشادات وتوجيهات مهمة .

1. ضرورة التزامك بما يلي :
  أ. **زي الكلية الرسمي .**   ب. **المعطف الابيض .**   ج. **القفازات ونظارات الامان (ان وجدت).**

2. يمنع منعاً مطلقاً الاكل والشرب والتدخين وادخال المأكولات والمشروبات في المختبر.

3. يمنع استخدام الهاتف المحمول (Mobil).

4. جميع المواد الكيميائية مواد ضارة لذا تعامل معها بحذر وعناية فائقة.

5. لا تنقل المواد الكيميائية أو الاجهزة خارج الأماكن المخصصة لها.

6. لا تستخدم فمك لملئ الماصة (Pipette).

7. لا تستخدم اداة زجاجية واحدة عند التعامل مع مادتين كيميائيتين مختلفة (لنقل أو تحضير أو تحريك), ولا تعيد ما تبقى من المواد المستخدمة الى القناني الاصلية لتلك المواد.

8. استخدم الوسيلة المناسبة عند حمل قناني المواد الكيميائية ((تجنب حملها من اعلاها فقط)).

9. لا تستخدم يديك لمسح المواد الكيميائية في حالة سقوطها.

10. لا تفتح قناني المواد الكيميائية بالقرب من اللهب.

11. تأكد من أسم المادة والصيغة الكيميائية للمادة المطلوبة قبل الاستعمال.

12. أخبر مشرف المختبر عند حدوث أي أمر طاريء (حريق, جرح, انسكاب مادة كيميائية ....الخ).

13. هنالك مواد كيميائية (تتسامى أو تبعث حرارة عند تحضيرها ....) , فيجب استخدام غرفة الغاز(HOOD).

14. قبل بدء العمل تعرف على محتويات المختبر (أماكن المواد الكيميائية المطلوبة والادوات المطلوبة للتجربة), بعد قراءة خطوات التجربة وجميع اجراءات الامان.

15. لا تقوم بتحوير خطوات التجربة إلا باستشارت المشرف.

يجب التعرف على خواص المواد التي تتعامل بها وكن حذر من:-

II. Quantitative Analysis

Table 1-1   Fundamental SI units

Quantity	Unit (symbol)	Definition
Length	meter (m)	One meter is the distance light travels in a vacuum during $\frac{1}{299\,792\,458}$ of a second.
Mass	kilogram (kg)	One kilogram is the mass of the prototype kilogram kept at Sèvres, France.
Time	second (s)	One second is the duration of 9 192 631 770 periods of the radiation corresponding to a certain atomic transition of ^{133}Cs.
Electric current	ampere (A)	One ampere of current produces a force of 2×10^{-7} newtons per meter of length when maintained in two straight, parallel conductors of infinite length and negligible cross section, separated by 1 meter in a vacuum.
Temperature	kelvin (K)	Temperature is defined such that the triple point of water (at which solid, liquid, and gaseous water are in equilibrium) is 273.16 K, and the temperature of absolute zero is 0 K.
Luminous intensity	candela (cd)	Candela is a measure of luminous intensity visible to the human eye.
Amount of substance	mole (mol)	One mole is the number of particles equal to the number of atoms in exactly 0.012 kg of ^{12}C (approximately $6.022\,141\,5 \times 10^{23}$).
Plane angle	radian (rad)	There are 2π radians in a circle.
Solid angle	steradian (sr)	There are 4π steradians in a sphere.

Table 1-2   SI-derived units with special names

Quantity	Unit	Symbol	Expression in terms of other units	Expression in terms of SI base units
Frequency	hertz	Hz		$1/s$
Force	newton	N		$m \cdot kg/s^2$
Pressure	pascal	Pa	N/m^2	$kg/(m \cdot s^2)$
Energy, work, quantity of heat	joule	J	$N \cdot m$	$m^2 \cdot kg/s^2$
Power, radiant flux	watt	W	J/s	$m^2 \cdot kg/s^3$
Quantity of electricity, electric charge	coulomb	C		$s \cdot A$
Electric potential, potential difference, electromotive force	volt	V	W/A	$m^2 \cdot kg/(s^2 \cdot A)$
Electric resistance	ohm	Ω	V/A	$m^2 \cdot kg/(s^2 \cdot A^2)$
Electric capacitance	farad	F	C/V	$s^4 \cdot A^2/(m^2 \cdot kg)$

Table 1-3   Prefixes

Prefix	Symbol	Factor	Prefix	Symbol	Factor
yotta	Y	10^{24}	deci	d	10^{-1}
zetta	Z	10^{21}	centi	c	10^{-2}
exa	E	10^{18}	milli	m	10^{-3}
peta	P	10^{15}	micro	μ	10^{-6}
tera	T	10^{12}	nano	n	10^{-9}
giga	G	10^{9}	pico	p	10^{-12}
mega	M	10^{6}	femto	f	10^{-15}
kilo	k	10^{3}	atto	a	10^{-18}
hecto	h	10^{2}	zepto	z	10^{-21}
deca	da	10^{1}	yocto	y	10^{-24}

Table 1-4   Conversion factors

Quantity	Unit	Symbol	SI equivalent^a
Volume	liter	L	$*10^{-3}m^3$
	milliliter	mL	$*10^{-6}m^3$
Length	angstrom	Å	$*10^{-10}m$
	inch	in.	$*0.025\ 4\ m$
Mass	pound	lb	$*0.453\ 592\ 37$ kg
	metric ton		$*1\ 000$ kg
Force	dyne	dyn	$*10^{-5}N$
Pressure	bar	bar	$*10^{5}Pa$
	atmosphere	atm	$*101\ 325$ Pa
	torr ($= 1$ mm Hg)	Torr	133.322 Pa
	pound/in.^{2}	psi	$6\ 894.76$ Pa
Energy	erg	erg	$*10^{-7}J$
	electron volt	eV	$1.602\ 176\ 53 \times 10^{-19}J$
	calorie, thermochemical	cal	$*4.184$ J
	Calorie (with a capital C)	Cal	$*1000$ cal $= 4.184$ kJ
	British thermal unit	Btu	$1\ 055.06$ J
Power	horsepower		745.700 W
Temperature	centigrade ($=$ Celsius)	°C	$*K - 273.15$
	Fahrenheit	°F	$*1.8(K - 273.15) + 32$

The Analytical chemistry

Analytical chemistry is the study of the separation, identification, and quantification of the chemical components (elements or compounds) of natural and artificial materials (sample), and the separation of components are often performed prior to analysis.

الكيمياء التحليلية فرع من فروع علم الكيمياء, فهو علم يختص بتحديد نوع وتركيب وكمية مكونات العينة (Sample), وبفصل مكونات العينة (المركبات والعناصر) وتعيين كميتها ونسبتها .

There are two types of chemical analysis:

A- Qualitative analysis:

Qualitative analysis gives an indication of the identity of the chemical species (elements or compounds) in the sample.

Example: If you have a solution, you obtained by extraction medical
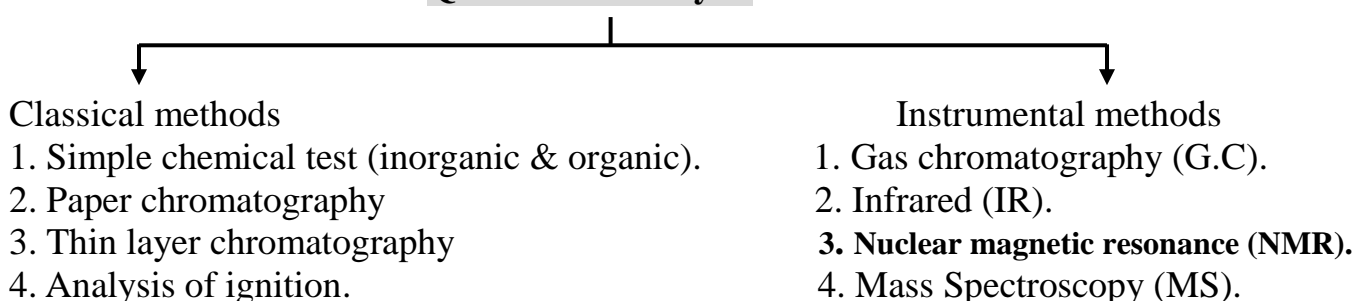
       1-Sugars   2-Poly saccharine   3-acids

B-Quantitative analyses:

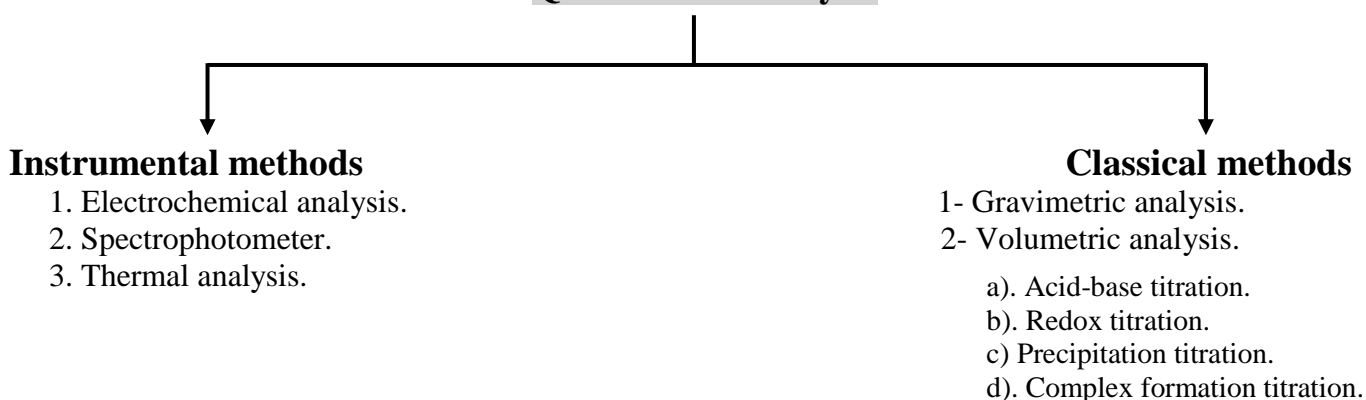Quantitative analysis determines the amount of certain components (elements or compounds) in the sample.

Example**:** In medicine it is important to know the level of drug in blood or urine.

Methods of analysis: **A. Classical methods**.   B. **Instrumental methods**.

Qualitative Analysis

Classical methods
1. Simple chemical test (inorganic & organic).
2. Paper chromatography
3. Thin layer chromatography
4. Analysis of ignition.

Instrumental methods
1. Gas chromatography (G.C).
2. Infrared (IR).
3. Nuclear magnetic resonance (NMR).
4. Mass Spectroscopy (MS).

Quantitative Analysis

Instrumental methods
1. Electrochemical analysis.
2. Spectrophotometer.
3. Thermal analysis.

Classical methods
1- Gravimetric analysis.
2- Volumetric analysis.

     a). Acid-base titration.
     b). Redox titration.
     c) Precipitation titration.
   d). Complex formation titration.

Experiment 1:
<u>Volumetric measurement glassware</u>

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

<u>**Note:**</u> The precision attainable with a burette is better than with measuring pipette.

2. Pipette: A piece of glassware used for measuring the volume of liquid comes in various sizes.

All pipettes are designed for transfer of known volumes of liquids from one container to another; we have two types of the pipettes:
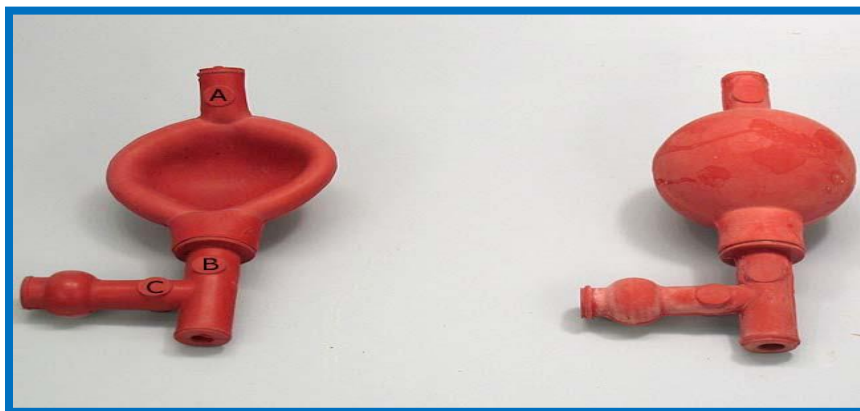
A-Volumetric or transfer pipette: Have one calibration mark and are used for deliver a single specific volumes or fixed volumes of liquid quite accurately.

B-A measuring or graduated or mohr pipette: It graduate along its length in convenient units it is used.

Name	Type	Function
Volumetric pipette	To Deliver (TD)	Delivery fixed volume
Mohr pipette	To Deliver (TD)	Delivery of a variable volume

<u>**Note**</u>: We always use bulb or aspirator fill pipettes
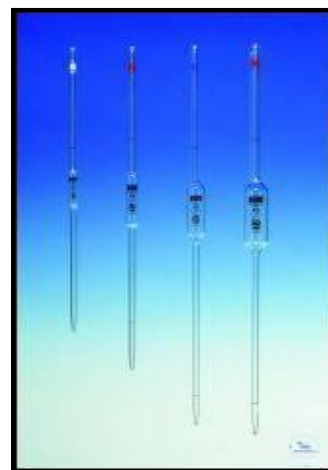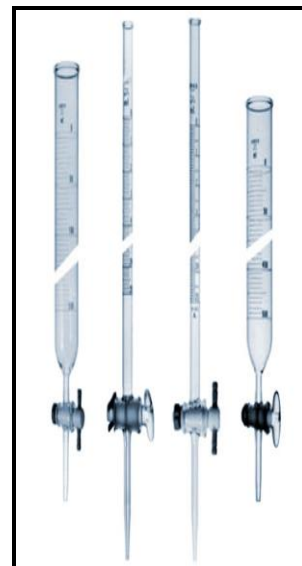
3. Graduated cylinder: A piece of glassware used for handling measure approximate volume of liquids.

> **Note:** Meniscus (concave) results when aqueous solution is measured in glass ware. It is dividing lines between liquid and air.

4. Volumetric flask:

A piece of glassware manufactured with capacities ranging from 5 ml to 5 liters and are usually calibrated to contain (TC) the specified volume when filled to the calibration ring (mark) on the nit neck , it is used in:

a- In prepare standard solution.

b- In dilution of the concentrated solution

5. Conical flask (Erlenmeyer flask): A piece of glassware come in various sizes used for:-

a- Titration: المعايرة ضمن منظومة تقدير تركيز المحاليل

b- Filtration: الترشيح

c- Distillation: التقطير (جمع السائل)

d- Heating and evaporation: التسخين والتبخير
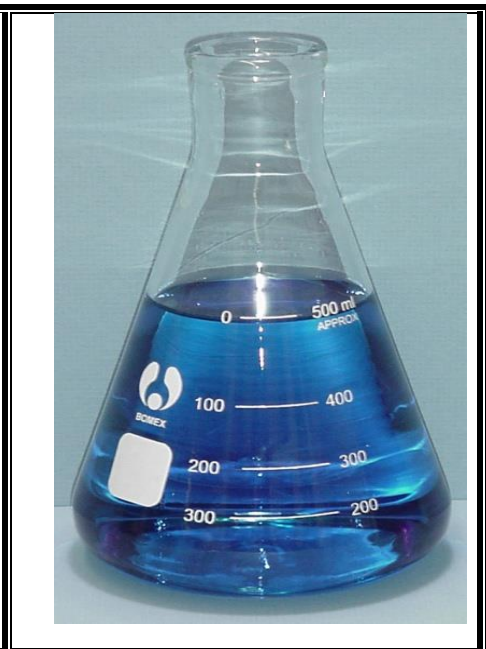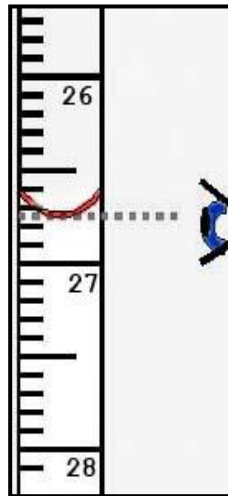
6-The beaker: A piece of glassware come in various sizes, used for:
a- Dissolving the samples   إذابة العينات
b- Transfer the solution   نقل المحاليل
c- Container of solution (for TC) حاوية محاليل
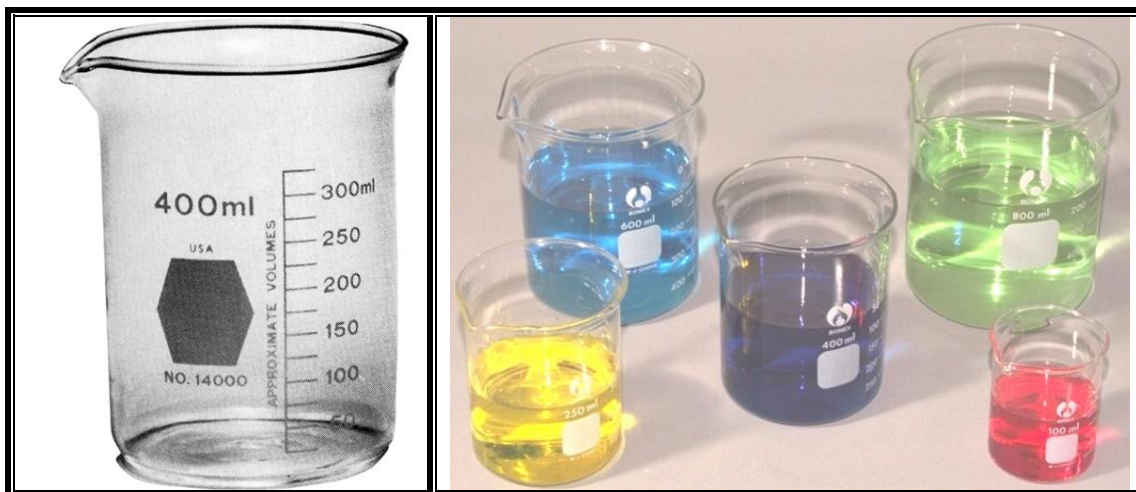
7. Stirring glass rod: A piece of glassware in various sizes, used for:
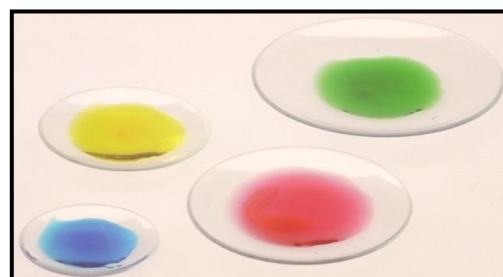a- In solubility mixed solute with solvent.
b- In decantation.
c- Collecting the precipitate.

8- Watch glass:
A piece of glassware in various sizes, using in:
 a. Weighing non-hygroscopic materials.
 b. Covering the beakers that contain heat solution.
 c. Covering the beakers during heat solution.

9- Spatula: A piece of laboratory tools used for transfer of solid material from a reagent bottle, manufactured from steel and ceramic materials.

10- Polyethylene wash bottle: A piece of laboratory tool used for washing the glassware, manufactured from polyethylene flexible, not affected by alkali solutions and HF.
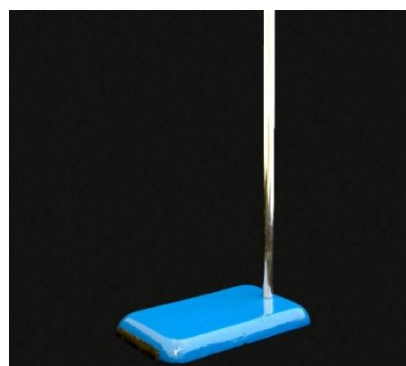

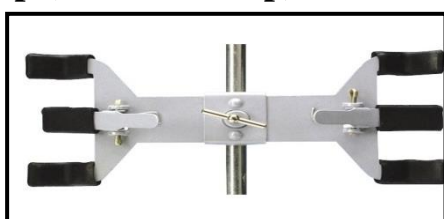**11- Brush:** A piece of laboratory tool used for cleaning the glassware in a various sizes.

12-Sensitive Balance:

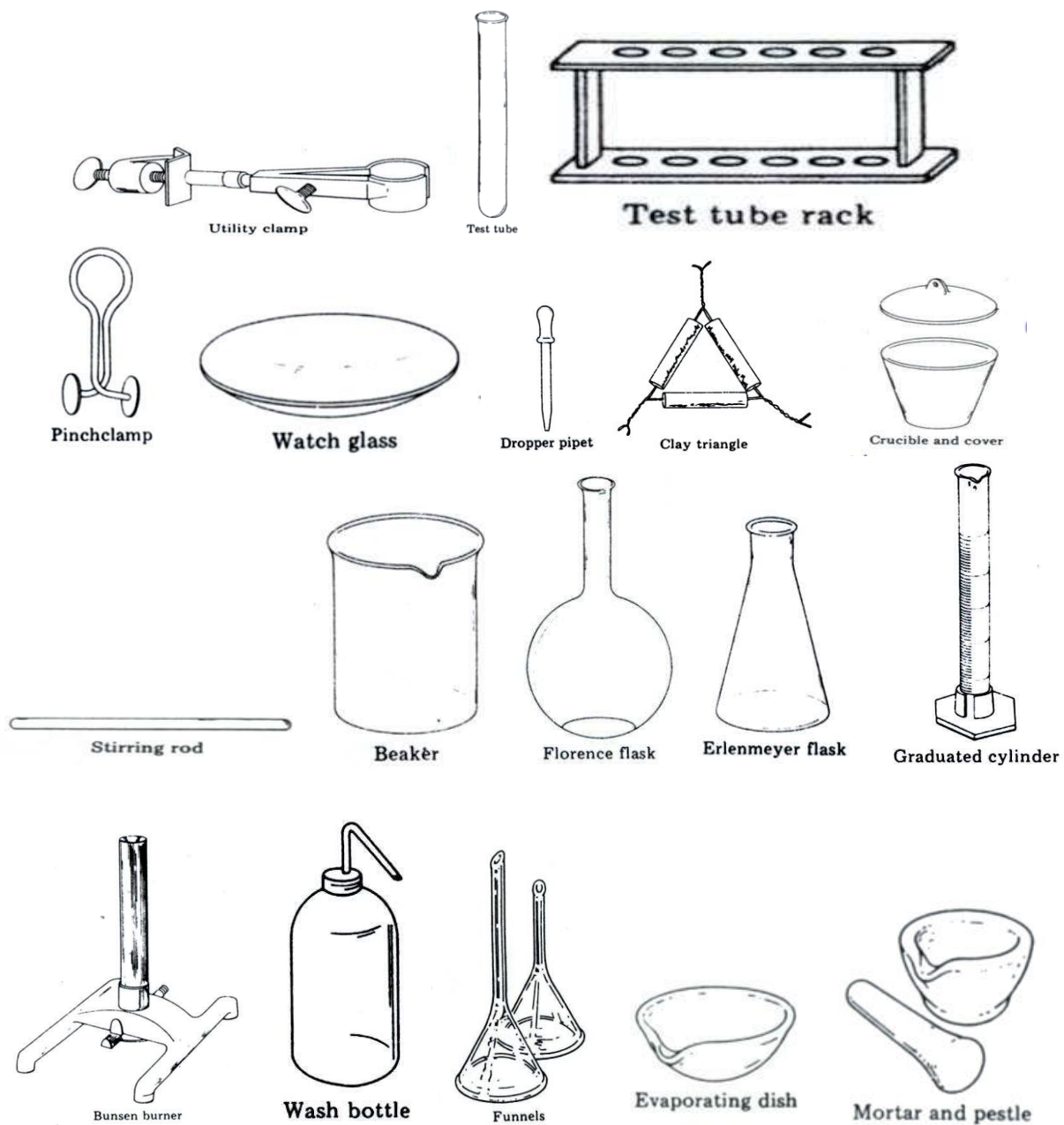**13- Stand:**

14-Clamp (Burette clamp):
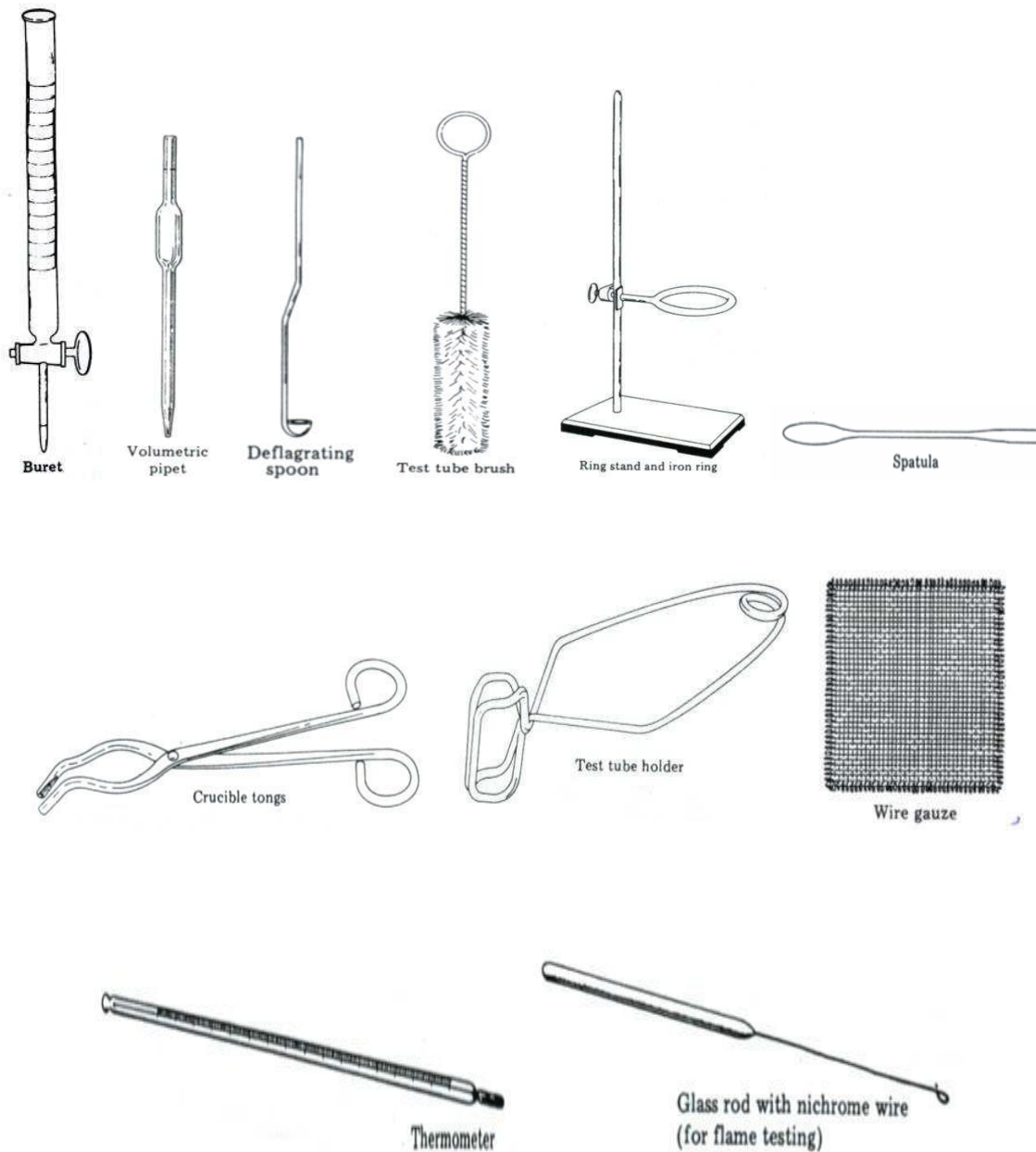
(Double Burette clamp)
15-Holder (Clamp holder):

16-Funnel: A piece of glassware used for:
a- Transfer the liquids.
b- In filtration.

LABORATORY GLASSWARE:-

Utility clamp

Test tube

Test tube rack

Pinchclamp

Watch glass

Dropper pipet

Clay triangle

Crucible and cover

Stirring rod

Beaker

Florence flask

Erlenmeyer flask

Graduated cylinder

Bunsen burner

Wash bottle

Funnels

Evaporating dish

Mortar and pestle

Buret

Volumetric
pipet

Deflagrating
spoon

Test tube brush

Ring stand and iron ring

Spatula

Crucible tongs

Test tube holder

Wire gauze

Thermometer

Glass rod with nichrome wire
(for flame testing)

Experiment 2
Laboratory Techniques

Handing Chemicals:

1-   Solids:

Solid chemicals are usually stored in wide-mouth bottles. Always check the label carefully before using any chemical. Remove the lid or stopper, place the lid or stopper so that it will not be contaminated, tilt the bottle and roll 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.
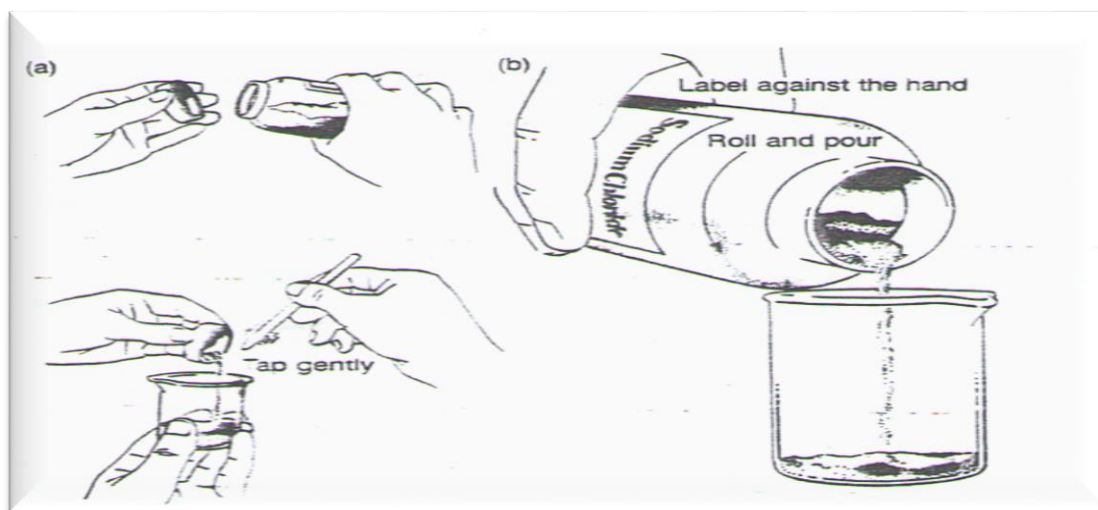

Figure1. Transfer of solid from a reagent bottle

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).
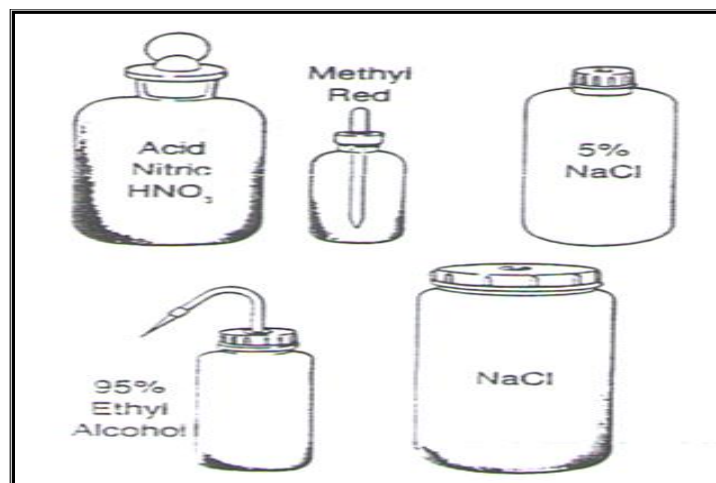

Figure2. Common reagent bottles for liquids and solids

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 use any liquid from the bottle. Careful checking of labels prevents many unnecessary accidents.
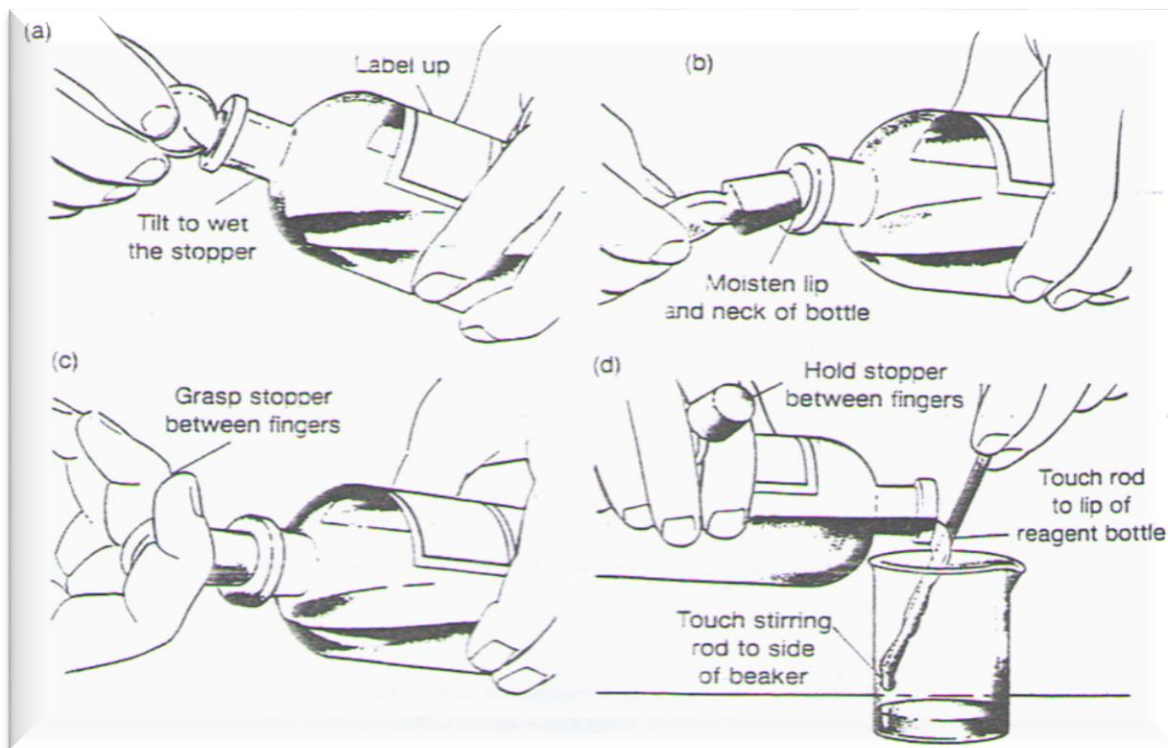

Figure3. Transferring liquid from a reagent bottle

**Experiments in General Chemistry**
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.

Figure4. Proper technique for reading a burette or a graduated cylinder

2- Using of Volumetric Pipettes:
Always use a pipette bulb or aspirator to fill pipettes. Volumetric pipettes have one calibration mark and are used to deliver specific volumes of liquids quite accurately.
The pipettes is rinsed with distilled water and then with small portions of the liquid to be measured. A small amount of the liquid
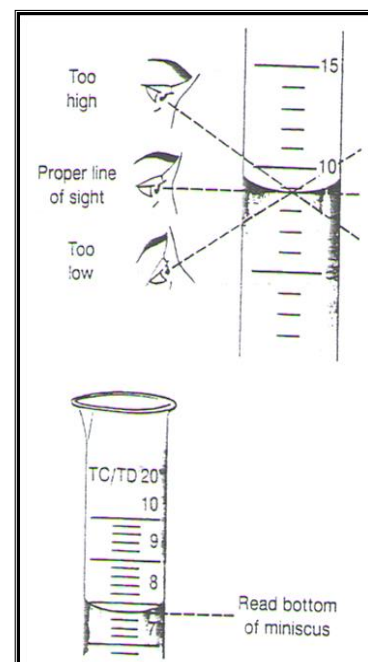
is drawn into the pipette. The pipette is held nearly horizontal and rolled so that the liquid comes in contact with the interior surface of the pipette. Finally, the liquid is allowed to drain through the tip. After the pipette has been rinsed with the liquid three times, liquid is drawn into the pipette until the liquid level stands above the calibration mark. The tip of the pipette 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 pipette 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 pipette, wait 20 seconds, touch the tip of the pipette to the (inside) surface of the container to remove the hanging drop and remove the pipette.

Do not blow out the last bit of liquid in the pipette. When the above instructions are followed the pipette will deliver the specified volume. Pipettes are available in a variety of sizes commonly, 5, 10, 25 and 50 mL, figure 5 illustrates the use of volumetric pipettes.
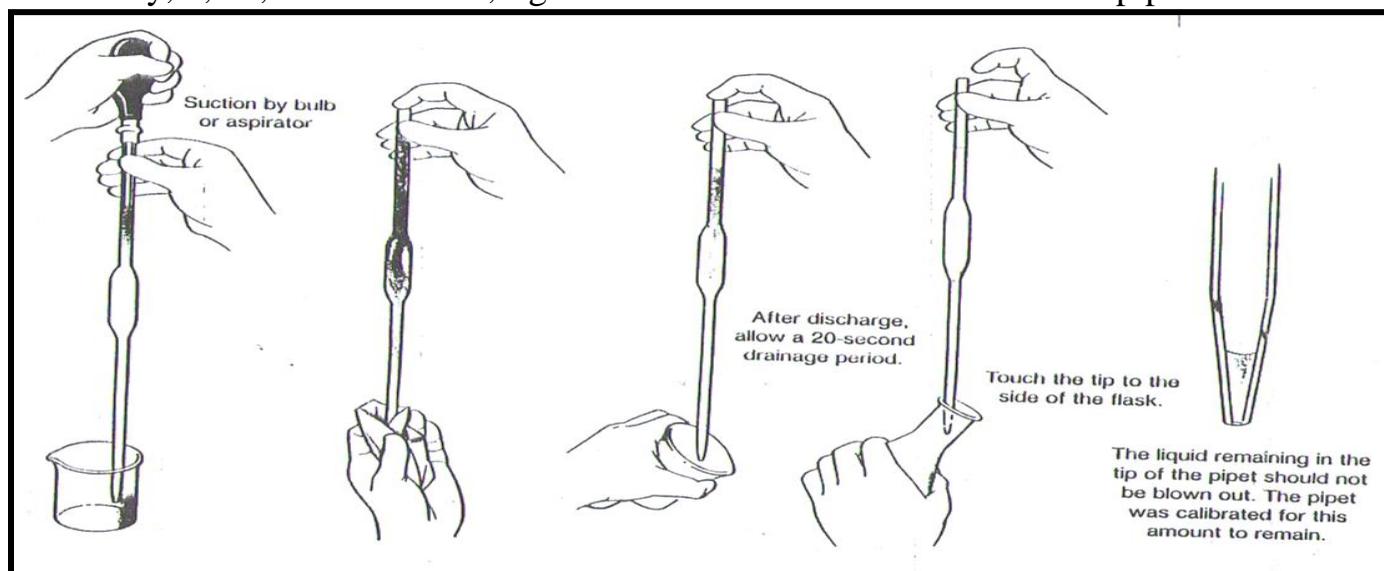

Figure5. Use of a volumetric pipette

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

3- Burettes and Titration Procedures:

Burettes are used to measure the volume of a liquid reagent required to reach with a carefully measured (liquid or solid) sample of another substance. Burettes 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 burette 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 burette. No water droplets adhere to the inner walls of a clean burette.

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

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.

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

A clean burette is rinsed with distilled water and then three times with approximately 5mL portions of the liquid to be measured, hold the burette nearly horizontally and rotate it so that the liquid comes in contact with all interior surfaces, the rinse liquid is then allowed to drain through the tip the burette 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 burette 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 burette until the desired reaction is complete, the burette 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 a conical flask (Erlenmeyer flask) (the receiving flask), the stopcock is used to control the rate at which the liquid in the burette, the titrant is added to the receiving flask (Figure6).

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.
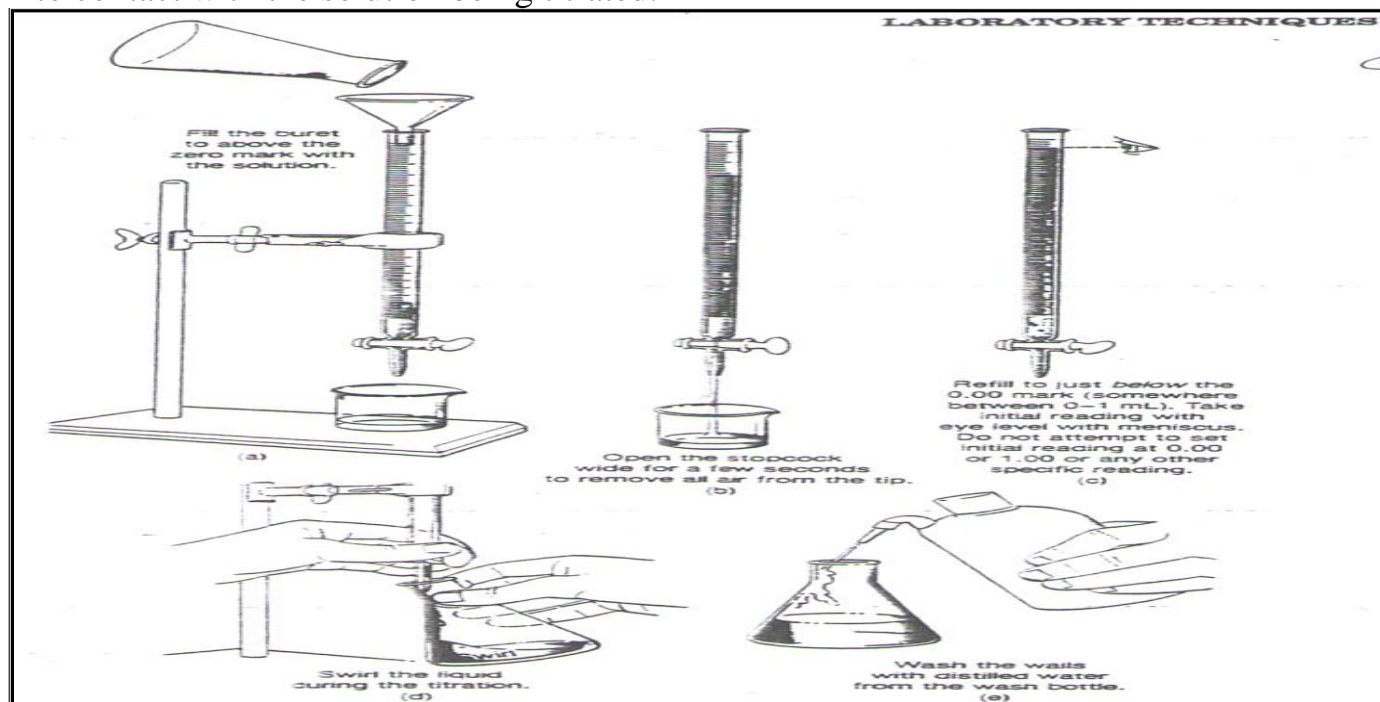

Figure6. Techniques of titration (a) Filling a burette (b) Operation of stopcock (c) Adding titrant (d) Swirling liquid (e) Washing wall of receiving flask

4- Volumetric Flasks:

Volumetric flasks are constructed to contain (not deliver) the volume specified on the flask, they are available in many sizes. Figure7 shows a volumetric flask and includes directions for its use.

(1) Place measured amount of solute in flask (2) Fill flask (with distilled water or solvent) 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
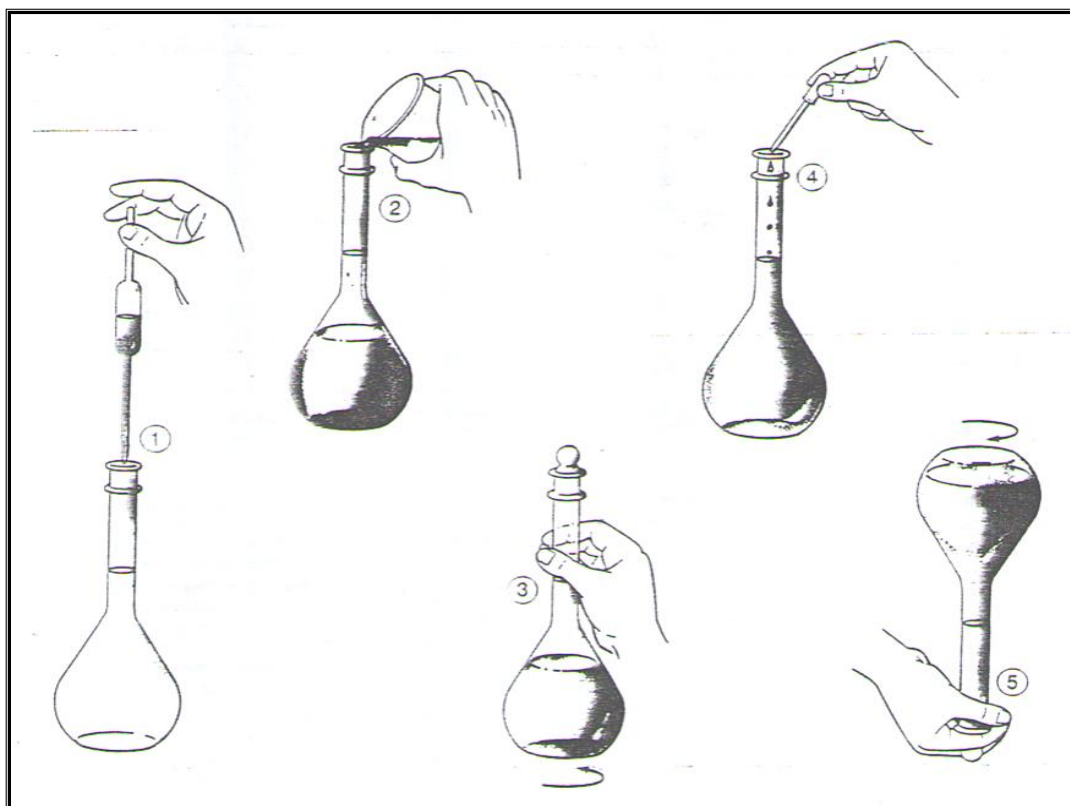

Figure7.   Use volumetric flask.

Experiment 3
Preparation & Standardization

Standardization: the process whereby the concentration of a standard solution is determined by titration of a primary standard.

Primary standard substances: These substances are obtainable in extraordinary pure form, primary standard reagents are available commercially, these have been carefully analyzed and the assay value is printed on the label. These regents have high purity used as the references material.

Standard solution: The reagent exactly known composition and concentration used in titration or any determination methods analysis.

The concentration of a standard solution is arrived in two ways:

1. From preparatory data obtained when a carefully weighed quantity of the pure reagent is diluted to an exactly known volume.
2. From data obtained by titration of a weighed quantity of a pure compound with the reagent.

The properties of primary standard materials: -

1. **It must be available in a highly pure state.**
2. **It must be stable in air (high stability).**
3. **It must dissolve easily in water (solvent).**
4. **It should have a fairly high relative molecular weight.**
5. **It should undergo a complete and rapid reaction.**

Chemicals are supplied in various grades of purity but for analytical work **AnalaR** grade primary standards must be used. **AnalaR** grade guarantees high purity.

Method for the Expression of concentration

Concentration: the term concentration refers to how much of one component of a solute is present in given amount of solution or solvent.

We need to discuss some of the terms by which chemists express the concentration of solutions; these include **F**ormal concentration, **M**olar concentration, **N**ormality and various types of percentage composition.

1. Formality or formal concentration (F)

The formality, of a solution expresses the number of gram- formula weights of solute present in one liter of solution, it follows that this term also gives the of milliformula weights of solute in one milliliter of the solution, the gram–formula weight (F.Wt.) is the summation of the atomic weights (in grams) of all the atoms appearing in the chemical formula.

$$F = \frac{Wt(g)}{FWt} \ x \ \frac{1000}{V(mL)} \quad \text{or} \quad F = \frac{no.m.FWt}{V(mL)}$$

$$no.m.FWt = \frac{Wt(mg)}{FWt}$$

Example Exactly (0.1753g) of NaCl is dissolved in sufficient H_2O to give (240 ml) of solution what is the formal concentration of NaCl?

Sol.: - F.Wt. for NaCl=35.44+23=58.44 g.f $^{-1}$

no. m. F.Wt. of NaCl = 0.1735 x 10^3 mg /58.44 g.f^{-1} = 3.00 mf

$$F = \frac{no.m.FWt}{V(mL)} = \frac{3mf}{240mL} = 0.0125 \quad f.L^{-1}$$

2. Molarity or molar concentration (M):

The molarity of a solution defines as the number of gram- molecular weights (or moles) of a species in one liter of solution, or the number of millimolecular weights in on milliliter of solution

$$M = \frac{Wt(g)x\ 1000}{M.Wt\ x\ V(mL)}$$

M.Wt = gram molecular weights = summation of atomic weights (in gram) of all atoms in molecular

Example: calculate the weight of (Na_2CO_3) you need to prepare (0.l M)in (250 ml) ?

Sol.: M.Wt of (Na_2CO_3) = 2(23)+12+3(16)= 106 g.mol^{-1}

$$M = \frac{Wt(g)x\ 1000}{M.Wt\ x\ V(mL)} = \frac{Wt(g)x\ 1000}{106g.mol\ x\ 250(mL)} = 0.1\text{mol.L}^{-1}$$

Wt. = 106g.mol^{-1} x 250mL x 10^{-3}L.mL^{-1} x 0.1mol.L^{-1} = 2.65 g.

Example: concentrated HCl has specific gravity of (1.185) and (38w/w) percent HCl

a-   How would you prepare?

b-   Find the molarity of the concentrated reagent?

$$M = \frac{sp.gr.x\left(\frac{w}{w}\right)\%x1000}{M.Wt.}$$

$$M = \frac{1.185x\ 38\%x1000}{36.5}$$

M= 12 mol.L^{-1} The molarity of concentrated HCl

3. Normality (N):

The normality of solution expresses the number of milliequivalents of dissolved solute contained in one milliliter of the solution, or the number of equivalents contained in on liter thus, a (0.20N) solution of silver nitrate contains (0.20) milliequivalent (meq) of this substance in each milliliter of the solution:

$$N = \frac{Wt(g)x\ 1000}{Eq.Wt\ x\ V(mL)}$$

$$N = \frac{sp.gr.x\left(\frac{w}{w}\right)\%x1000}{Eq.Wt.}$$

Equivalent weight of chemicals: -

The definition of the equivalent weight for a chemical compound always refers to a specific chemical reaction evaluation of this quantity is impossible without knowledge of the nature of this reaction, always: -

$$\boldsymbol{Eq.Wt.} = \frac{\boldsymbol{M.Wt.}}{\boldsymbol{n}}; \quad n = \text{Equivalence}$$

For: -

a). Acids equal a no. of H^+ ions that react.

1. Inorganic acids n = no. of H in formula (**HCl=1; HNO₃=1; H₃PO₄=3; H₂SO₄=2; H₂CO₃=2**).

2. Organic acids n = no. of –COOH in formula (**CH₃COOH=1; HOOC-CH₂-CH₂-COOH=2**).

b). Bases equal a n =no. of OH^- ions that react (**NaOH =1; NH₄OH=1; Al(OH)₃=3; Ba(OH)₂=2**).

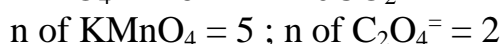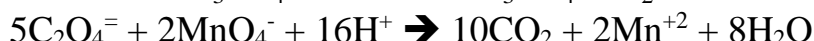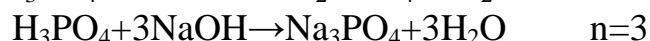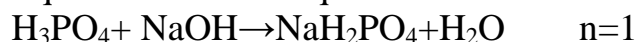**c). Salts** equal a no. of metals ion multiplied by the number of its oxidants:-

{**NaCl, KI, AgNO₃=1**}; { **Na₂CO₃, Ca(NO₃)₂ , BaSO₄, CaHPO₄ = 2**};{**Na₃PO₄, Al(NO₃)₃ , Na₃AsO₄ = 3**};

Ca₃(PO₄)₂= 6 ; Al₂(SO₄)₃ =6; NaHCO₃ = 1

d). Redox reagents equal a no. of electron moles in reaction or the change in oxidation number of reagent:

$$Fe^{+3} + e^- \rightarrow Fe^{+2} \qquad n = 1$$
$$Sn^{+2} \rightarrow Sn^{+4} + 2e^- \qquad n = 2$$
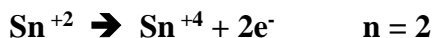
e). Ions equal a no. of ion charge: (**Na⁺,NO₃⁻,HCO₃⁻,H₂PO₄⁻,K⁺=1**),(**Ca⁺²,Mg⁺²,SO₄⁻²,CO₃⁻²=2**)
  (**PO₄ ⁻³, Al⁺³ = 3**)

For all reactions, from chemical equation balanced equal the number of moles of the substance interacting with it:

$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O \qquad n=1$$
$$H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O \qquad n=2$$
$$H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O \qquad n=3$$
$$5C_2O_4^= + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{+2} + 8H_2O$$
$$n \text{ of } KMnO_4 = 5 \text{ ; } n \text{ of } C_2O_4^= = 2$$

4. Percent Concentration:

The percentage composition of solution can be expressed in any of several ways, three of the more common methods are defined as fallow: -

a)   **Weight percentage:**   Wt. % = (Wt. of solute / Wt. of solution) x100
b)   **Volume percentage:**   V. % = (V. of solute / V. of solution) x100
c)   **Weight Volume percentage:**   (Wt./ V) % = (Wt. of solute / V. of solution) x100

Notes: -

➤ $V_{solution} \neq V_{solvent} + V_{solute}$;
➤   (Wt./V) % = (Wt.%) D $_{solution}$;
➤   (Wt./V) % = (V.%) D $_{solute}$;
➤   The unit volume (mL) should be unity of the mass (g), although the unit (L) shall be mass unit (Kg).
➤   D $_{solution}$ density of solution, D $_{solute}$ density of solute, or specific gravity (sp.gr.)
➤   The denominator in each equation refers to the solution and not to the solvent alone.
➤   The first two expressions are independent of the units of volume or weight in their definition whereas third is not.
➤   Weight percent has the great advantage of being independent of temperature, for this reason it is widely used.
➤   The concentrations of commercial aqueous reagents are frequently expressed in terms of weight percent- thus concentrated nitric acid is solution.
➤   Weight Volume percent is frequently used to indicate the concentration of dilute aqueous solutions of solid reagents: Thus a 5 percent silver nitrate solution is prepared by dissolving (5 g m) of silver nitrate in water and diluting to 100 mL.

5. Parts per solution: -

In expressing the concentration of very dilute solutions, percentage compositions become use because the zeros number need to place decimal point, under the circumstances the concentration is more conveniently expressed in parts per solution, as fellow:

$$\text{Part Per Thousand:- } (ppt = \frac{Wt.of\ solute(g)}{V\ of\ solution(L)}) \text{ or } (ppt = \frac{Wt.of\ solute(g)}{Wt\ of\ solution(Kg)})$$

$$\text{Part Per Million:- } (ppm = \frac{Wt.of\ solute(mg)}{V\ of\ solution(L)}) \text{ or } (ppm = \frac{Wt.of\ solute(mg)}{Wt\ of\ solution(Kg)})$$

$$\text{Part Per Billion:- } (ppb = \frac{Wt.of\ solute(\mu g)}{V\ of\ solution(L)}) \text{ or } (ppb = \frac{Wt.of\ solute(\mu g)}{Wt\ of\ solution(Kg)})$$

$$1Kg = 1000g = 1000000mg = 1000000000\mu g$$

The Dilution: -

It may necessary to prepare a dilute solution of specified concentration from a more concentration solution of known concentration by adding pure solvent to it, we can define dilution as a procedure used to prepare a solution with a less concentration from more concentrated solution.

The key to understanding dilution is to remember that adding more solvent to a given amount of solution do not change solute amount present in solution (grams, moles & equivalents).

Moles of solute before dilution = Moles of solute after dilution

$$C_1 \times V_1 = C_2 \times V_2$$

C = Concentration (M, N, ppt, ppm, ppb)

V = Volume (L or mL)

This do not change upon dilution to final solution volume, because only solvent (not solute) is being added, thus

$$C_2 = C_1 \times V_1 / V_2$$

Note that V_2 always larger than V_1, and $C_2 < C_1$ always lesser than C_1.

Mixing concentration solution (W%=a%) with concentration solution (W%=b%) resulting solution concentration (W%=c%), If a> b, the a> c> b.
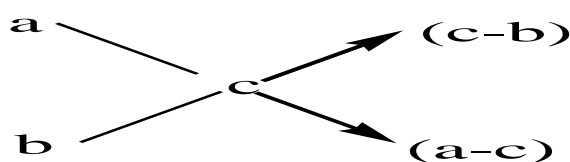
Example: How is the preparation of a solution containing 40% of nitric acid from concentrate nitric acid (W%= 96%), density (d = 1.495 g.mL^{-1} or sp.gr.)?

Sol.:-
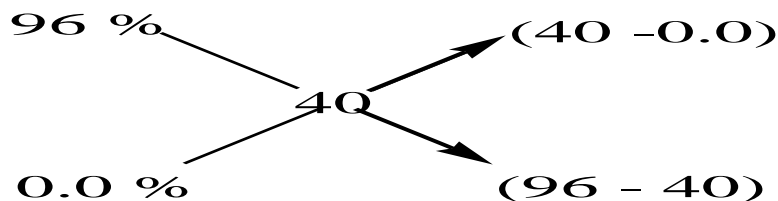
Take 40 g of HNO$_3$ 96%, with 56 g distilled water (56mL), we get 40% of HNO$_3$

$$d = Wt. (g) / V (mL)$$

$$V = Wt / d = 40g / 1.495 \text{ g.mL}^{-1} = 26.76 \text{ mL of } HNO_3 \text{ 96\%,}$$
Dilute ratio 26.76: 56

Example: How to Prepare a solution of 80% nitric acid (d= solution from (W%=75%, d=1.452g.mL^{-1}) and another (W%=96%, d=1.495g.mL^{-1})? (**H.W.**)

The Titration: -

One of the most important techniques an analytic chemistry is "titration", the addition of a carefully measured volume of one solution containing substa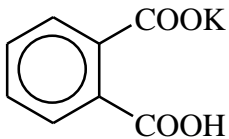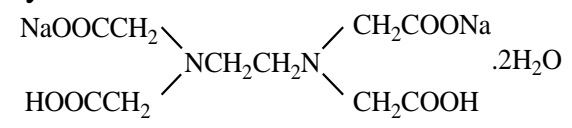nce (A) in known concentration, to a second solution containing substance (B) in unknown concentrate, with which it will react quantitatively, the solution of known concentration used in titration is called a **standard solution**, the goal of every titration is the addition of standard solution in an amount that is chemically equivalent to substance (solution B) with which it reacts, this condition is achieved at the equivalent point, completion of reaction at the (end point) is signaled by change in some physical properties of solution at or near the end point such as color due to reagent indicator substance or formation precipitation.

➢   Simple and easy.
➢   Fast and can be done on site.
➢   Less expensive.
➢   Estimation of content or Assay.
➢   Precise and accurate.

    Some examples of acids, bases, oxidising, reducing and complexing agents used as primary standards are outlined in the following table.

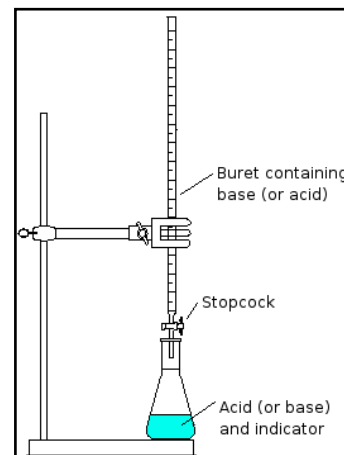| Primary standard	Examples
Acid	Hydrated oxalic acid, $(COOH)_2.2H_2O$ Potassium hydrogenphthalate:
Base	Anhydrous sodium carbonate, Na_2CO_3
Oxidising agent	Potassium dichromate, $K_2Cr_2O_7$ potassium iodate, KIO_3
Reducing agent	Sodium oxalate, $(COONa)_2$
Complexing agent	Hydrated disodium salt of EDTA

Chemicals are supplied in various grades of purity but for analytical work **AnalaR** grade primary standards must be used. **AnalaR** grade guarantees high purity.

TYPES OF TITRATION

1-   Acid base titration.
2-   Oxidation-reduction titration.
3-   Precipitation titration.
4-   Complex-formation titration.
     We use different types of indicators according to the nature of reactions.
- Burette must be vertical, use and then remove funnel, check meniscus, rinse with distal water and then given solution.
- In using a Pipette rinse with distal water first and then with given solution. Check meniscus. Do not blow out remainder of liquid into flask and keep tip of pipette in contact with flask.
- Conical flask should not be rinsed with solution it is to contain and swirl.
- In using a volumetric flask, the last few mL must be added so that the meniscus rest on calibration mark.
- Invert stoppered flask to ensure solution is homogeneous/uniform
Why is a conical flask, rather than a beaker, used in the experiment?
- To allow easy mixing of the contents, by swirling.
Why is the funnel removed from the burette after adding the acid solution?
- So that drops of solution from the funnel will not fall into the burette.
- In using a burette, it is important:-
(a) to rinse it with a little of the solution it is going to contain.
- To remove any residual water, and so avoid dilution of the acid solution when it is poured into the burette.
(b) to clamp it vertically.
- To enable the liquid level to be read correctly.
(c) to have the part below the tap full?
- To ensure that the actual volume of liquid delivered into the conical flask is read accurately.
The following procedures were carried out *during* the titration: -
1-   The sides of the conical flask were washed down with distal water.
2-   The conical flask was frequently swirled or shaken.
Give one reason for carrying out each of these procedures?
- To ensure that all of the acid added from the burette can react with the base.
- To ensure complete mixing of the reactants.
Why is a rough titration carried out?
- To find the approximate end-point. This information enables the subsequent titrations to be carried out more quickly.

Why is more than one accurate titration carried out?
- To minimise error by getting accurate readings within 0.1 mL of each other.

Indicators: -

Indicators are compounds that allow us to detect the end-points of titrations. Typically, they undergo an abrupt colour change when the titration is just complete. In general, an indicator reacts in a similar manner to the substance being titrated and so indicator choice will depend on the titration type: acid–base, redox, complexization or precipitation.

An **acid–base indicator** is normally a weak organic acid that will dissociate in aqueous solution, establishing the following equilibrium:

$$HIn\ (aq) + H_2O(l) \longleftrightarrow H_3O^+(aq) + In^-(aq)$$
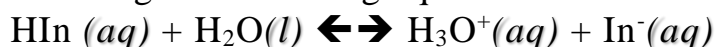
It is able to act as an indicator because it has one colour in its acid form (HIn) and a different colour in its conjugate base form (In⁻).

If we examine the following table in which the properties of a selection of some common indicators are presented, we see that an acid–base indicator changes colour over a range of about 2 pH units and not at a specific pH

Indicator	HIn colour	pH range of colour change	In⁻ colour
Bromophenol blue	Yellow	3.0 – 4.6	Blue
Methyl red	Red	4.2 – 6.3	Yellow
Bromothymol blue	Yellow	6.0 – 7.6	Blue
Phenol red	Yellow	6.8 – 8.4	Red
Phenolphthalein	Colourless	8.3 – 10.0	Pink

Choosing an indicator for a titration depends on the type of acid–base reaction taking place. There are four different types and these are outlined in the following table together with the pH values at their equivalence points.

Acid–base reaction type	pH at equivalence point
Strong acid/strong base	7
Weak acid/strong base	>7
Strong acid/weak base	<7
Weak acid/weak base	~7

It is important when carrying out an acid–base titration that only a few drops (two or three) of indicator are used.

The reason is that they are weak acids and so are themselves capable of being neutralized by bases.

Hence the more indicator we use, the greater will be the volume of base needed to neutralize it and so the less accurate the titration volume will be.

A **redox indicator** can be an oxidizing agent or a reducing agent and it can signal the end-point of a redox titration because it has one colour in its reduced state and a

different colour in its oxidized state. One common redox indicator is ferroin: it has a colour change from pale blue in its oxidized state to red in its reduced state.

In complexization titrations, the end-points are detected by means of **metal ion indicators**. These are organic dyes which form coloured complexes with metal ions and to be suitable as indicators they must bind less strongly with metal ions than the complexing agent does.

Indicator Choice for Minimization of Titration Error: -

The difference between the equivalence point and the end point (the titration error) should be minimal if accurate results are to be obtained. The choice of indicator is critical in this process as illustrated above.

Calculation of Results from titration;

The balance of the titration is chemical equation balanced, to determine the concentration of unknown solution by standard solution, (the equivalents of unknown equal to the equivalents of standard), for general reaction:-

$$aA + bB \rightarrow cC + dD$$
$$\text{no. Eq. of A} = \text{no. Eq. of B}$$
$$\text{no. Eq.} = N \times V = Wt. / Eq. Wt.$$
$$N_A \times V_A = N_B \times V_B$$
$$\text{Eq. Wt. of B} = M.Wt. / a$$
$$\text{Wt. of B} = \frac{N_A \times V_A \times M.Wt. \text{ of } B}{a}$$
$$\frac{V_A M_A}{a} = \frac{V_B M_B}{b}$$
$$\text{Wt\% of B} = \frac{Wt. \text{of } B}{Wt. \text{of sample}} \times 100$$

Example: A solution of Ba(OH)₂ was standardized by titration against (0.1280N)HCl. Exactly (31.76 mL) of the Base were required to neutralize (46.25 ml) of the acid what is the normality of the Ba(OH)₂ solution? At the end point in the titration we assume that

$$\text{no.meq Ba(OH)}_2 = \text{no.meq HCl}$$
$$(V)ml_{Ba(OH)_2} \times N_{Ba(OH)_2} = (V)ml_{HCl} \times N_{HCl}$$
$$\mathbf{31.76 \times N_{Ba(OH)2}} = 46.25 \times 0.1280$$
$$\mathbf{N_{Ba(OH)2}} = \frac{46.25 \times 0.1280}{31.76} = \mathbf{0.1864 \text{ eq.L}^{-1}}$$

Example: A quantity of BaCl₂.2H₂O is to be titrated with silver nitrate solution, the number of milliequivalents contained in (0.367g) of pure BaCl₂.2H₂O is sought

$$\text{No. meq. Of (A)} = \frac{Wt \text{ of } (A) (mg)}{Eq.Wt \text{ of } (A)}$$
$$\mathbf{Eq.Wt. \text{ of (BaCl}_2.2H_2O)} = \frac{M.Wt. \text{of } (A)}{n} = \frac{244g/mol}{2 \text{ } eq/mol} = \mathbf{122 \text{ g.eq}^{-1}}$$
$$\mathbf{No. \text{ meq. Of (BaCl}_2.2H_2O)} = \frac{0.367 \times 1000 (mg)}{122 mg/meq.} = \mathbf{3.01 \text{ meq.}}$$

Experiment 4
Titration of Sodium Carbonate with Hydrochloric acid
(Acid – Base Titration)

Theory: -

Hydrochloric acid can produce chlorine gas in reactions and liberate hydrogen when exposed to air, therefore its **nonstandard solution;** standardization of HCl using standard solution of sodium carbonate, to calculate concentration of HCl, the equations reaction described by two steps: -
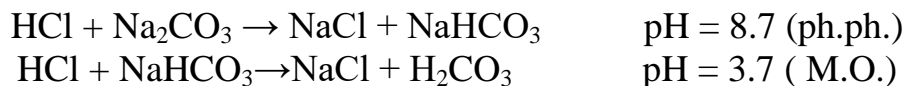
$$HCl + Na_2CO_3 \rightarrow NaCl + NaHCO_3 \qquad pH = 8.7 \ (ph.ph.)$$
$$HCl + NaHCO_3 \rightarrow NaCl + H_2CO_3 \qquad pH = 3.7 \ (M.O.)$$

Apparatus used: -
- Burette.
- Conical flask.
- Beaker.
- Pipette.
- Funnel.
- White tile.

Procedures:
1. Transfer 5 mL Na_2CO_3 solution into C.F.
2. Add 2-3 drops of ph. ph. (pink color); or MO (yellow).
3. Titrate using HCl till (colorless); or in use MO (pink color).
4. Repeat steps 1, 2, and 3, at least 2 or 3 times, (DV=± 0.1mL)
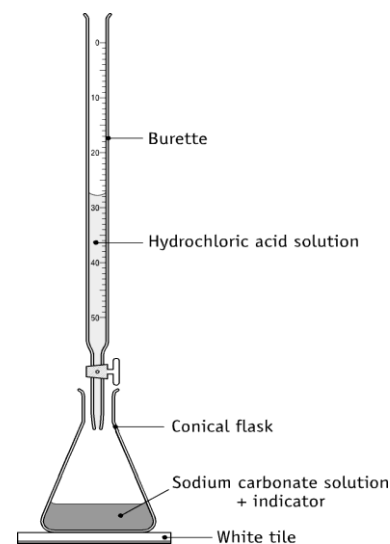
Calculation:

Calculate the average of V. of HCl
Calculate the Normality of HCl by
$$(N \times V) \ HCl = (N \times V) \ Na_2CO_3$$

Notes: -
1. In case ph. ph.; the ratio reaction 1:1 mole of HCl.
2. In case MO; the ratio reaction 1:2 mole of HCl.

Experiment 5
Titration of Sodium Hydroxide with Hydrochloric acid
(Acid – Base Titration)

Theory: -

Sodium hydroxide react with carbon dioxide and absorbs water from the air, therefore its nonstandard solution; standardization of NaOH using 2nd standard solution of HCl, to calculate concentration of NaOH, the equations reaction described by: -
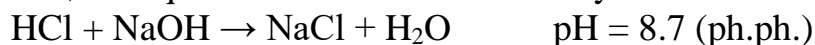
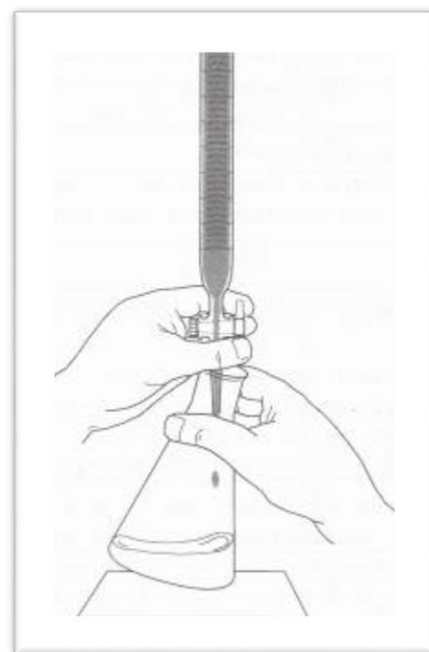$$HCl + NaOH \rightarrow NaCl + H_2O \qquad pH = 8.7 \text{ (ph.ph.)}$$

Apparatus
used:-
* Burette.
* Conical flask.
* Beaker.
* Pipette.
* Funnel.
* White tile.

Procedures:
1. Transfer 5 mL NaOH solution into conical flask.
2. Add 2-3 drops of ph. ph. (pink color).
3. Titrate using HCl till (colorless).
4. Repeat steps 1, 2, and 3, at least 2 or 3 times, (DV=$\pm$ 0.1mL)

Calculation:

Calculate the average of V. of HCl
Calculate the Normality of NaOH by
$$(N \times V) \, HCl = (N \times V) \, NaOH$$

Burette

Hydrochloric acid solution

Conical flask

5mL of NaOH
+ indicator

White tile

Experiment 6
## Titration of mixture (Sodium Carbonate + Sodium hydroxide) with Hydrochloric acid
(Acid – Base Titration)

Theory: -

Sodium hydroxide react with carbon dioxide and absorbs water from the air, therefore its content sodium carbonate and sodium bicarbonate (mixture); to calculate concentration of mixture contents titrated with HCl standard, the equations reaction described by two steps: -

5. $HCl + X\ Na_2CO_3 \rightarrow X\ NaCl + X\ NaHCO_3$ pH = 8.7 (ph.ph.)

            $Y\ NaOH \rightarrow Y\ NaCl + YH_2O$ pH = 7 (ph.ph)

6. $HCl + X\ NaHCO_3 \rightarrow X\ NaCl + X\ H_2CO_3$ pH = 3.7 (M.O.)

Apparatus

used: -

- Burette.
- Conical flask (C.F.).
- Beaker.
- Pipette.
- Funnel.
- White tile.

Procedures:

1. Transfer 5 mL **mixture** solution into C.F.
2. Add 2-3 drops of ph. ph. (pink color).
3. Titrate using HCl till ph. ph.(colorless); Calculate V_1 of HCl.
4. Add 2-3 drops of MO (yellow).
5. Titrate using HCl till MO (pink color); Calculate V_2 of HCl.
6. Repeat steps 1, 2, 3, 4 and 5, at least 2 or 3 times, (DV=± 0.1mL).

Calculation:

Calculate the average of V_1 & V_2 of HCl

Calculate the Normality of Carbonate and NaOH by

$(N \times V_1)\ HCl = (\frac{1}{2}\ N \times V)\ Na_2CO_3 + (N \times V)\ NaOH$

$(N \times V_2)\ HCl = (\frac{1}{2}\ N \times V)\ Na_2CO_3$

Notes: -

1. In case ph. ph.; the ratio reaction of carbonate 1:1 mole of HCl only.
2. In case MO; the ratio reaction of carbonate 1:2 mole of HCl and the ratio reaction of bicarbonate 1:1 mole of HCl.

Experiment 7
Standardization of potassium permanganate using oxalic acid
(Reduction-Oxidation Titration)

Theory:

Oxidation means loss of electron(s) and reduction means gain of electron(s); reactions where a transfer of electrons is involved are thus called oxidation-reduction (redox) reactions, in addition to neutralization (acid-base) and precipitation reactions, the redox processes can be utilized in quantitative titrimetric chemical analysis.

KMnO$_4$ is always used for standard solutions, this utilizes the high oxidation performance of this compound, the majority of titrations are carried out under strongly acidic solutions (but not in HCl, which is oxidized to chlorine and chlorine dioxide and would therefore interfere, also HNO$_3$); In strongly acidic solutions, Mn(VII) is reduced to Mn(II):

$$KMnO_4 + C_2O_4H_2 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + CO_2 + H_2O$$

Conditions for KMnO4 titration:

1. Acidic medium using 20 ml 2N H$_2$SO$_4$; **Why should you avoid HNO$_3$ and HCl?**
   2. Heating to 70°C (**not boiling, why?**)

Procedures

1. Transfer 10 ml oxalic or oxalate soln. in C.F.
2. Add 20 ml 2N H$_2$SO$_4$.
3. Heat to 70°C.
4. Titrate with KMnO$_4$ gradually with stirring till pink color.
5. Repeat steps 1, 2, 3 and 4, at least 2 or 3 times, (DV=± 0.1mL).

Calculate: -

Calculate the average of V. of KMnO$_4$
Calculate the Normality of KMnO$_4$ by
(N x V) KMnO$_4$ = (N x V) Oxalic acid

Discuss and answer: -

- How to balance the redox Equation?
- KMnO$_4$ is a 2nd standard substance, why?
- In this titration don't use indicator, why?
- Define: Oxidation; Reduction; Oxidizing agent, and Reducing agent?

Burette

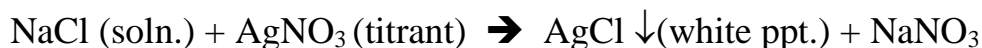KMnO4 Solution

Conical flask

Oxalic or Oxalate solution

White tile
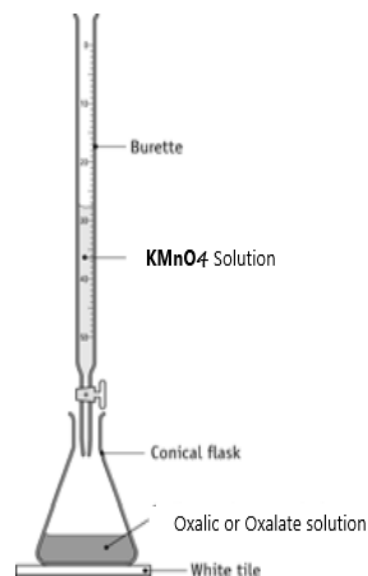
Experiment 8
Silver nitrate titrations by Mohr method
(Precipitation titration)

Theory:

Certain combinations of aqueous cations and anions produce insoluble products (precipitates); e.g.: $AgNO3$ (aq.) + NaCl (aq.) → AgCl (s) ↓ + $NaNO3$ (aq.)

Ionic:- $Ag^+ + Cl^- →$ AgCl↓
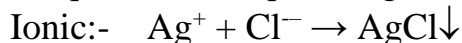
This reaction can be employed for quantification of chloride ions in unknown solution by means of titration with silver nitrate solution of known concentration. This technique, called Mohr method, uses chromate K_2CrO_4 as an indicator. Chromate forms also an insoluble salt with Ag ion. How, then, can it be used as an indicator? Simply stated, AgCl is less soluble than Ag_2CrO_4. Initially the Ag^+ ions (the titrant) enter the solution where there is an excess of chloride ions, and all the silver ions are being consumed for formation of the white precipitate of AgCl. When the equivalence point is reached, the Cl– ions are no longer available, and the Ag^+ concentration is allowed to rise to the point where the red-brown insoluble Ag_2CrO_4 appears:-

NaCl (soln.) + $AgNO_3$ (titrant) ➔ AgCl ↓(white ppt.) + $NaNO_3$

At the end point:- $AgNO_3$(titrant) + K_2CrO_4 ➔ KNO_3 + Ag_2CrO_4 ↓(red ppt.)

This method (**Argentometry**) can be used for determination of halides (Cl^-, Br^-, I^-), mercaptans (thioalcohols), fatty acids and several divalent anions.

Another similar approach is called mercurimetry. In this case the titrating reagent contains mercury (II) ions that react with chloride in the sample to produce soluble but non-dissociated mercury (II) chloride, $HgCl_2$. The indicator in this case is sodium nitroprusside $Na_2[Fe(CN)_5NO]$. The appearance of free Hg^{2+} ions at the point of equivalence results in formation of white precipitate of mercury (II) nitroprusside.
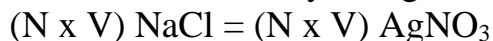
Procedure:

1- Transfer 10 ml of NaCl solution in C.F.
2- Add 3 drops of chromate indicator pH (6.5-9).
3- Titrate against 0.1N $AgNO_3$ (white ppt. is formed).
4- At end point the excess of $AgNO_3$ will react with Ind.; To form red ppt.
5- Repeat steps 1, 2, 3 and 4, at least 2 or 3 times, (DV=± 0.1mL).

Calculations:

Calculate the average of V. of $AgNO_3$
Calculate the Normality of $AgNO_3$ by
(N x V) NaCl = (N x V) $AgNO_3$

-      $AgNO_3$ is a 2nd standard substance, why?

<div align="center">

Experiment 9
Complex-formation titration
</div>

Theory:

In a complex-formation titration the reaction between the analyte and the titrant involves complex formation. EDTA, Ethylene Diamine Tetraacetic Acid (disodium edentate VS), can be used to analyse metal ions with which it forms 1:1 complexes. EDTA is a multidentate ligand.

A ligand is an atom or group of atoms that can bind to another atom by forming **coordinate** (or dative) **bonds**, to function as a ligand, the atom must possess a pair of non-bonding electrons that it can share with the other atom prepared to accept them, in alkaline conditions, EDTA has six such atoms (four oxygen atoms and two nitrogen atoms) through which it binds to the metal ions, so EDTA is a hexadentate ligand, if two or more electron pairs of a multidentate ligand form coordinate bonds to the central atom, the resulting complex is called **a chelate**.

When EDTA is used in complex-formation titration, a metal ion indicator is used, a metal ion indicator changes color when it binds to a metal ion, for the metal ion indicator to be useful in these types of titrations it must bind to the metal loosely so that the following process can take place.

<div align="center">

M-In + EDTA ➔ M-EDTA + In
Color I   color II
</div>
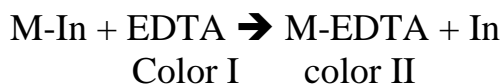
Murexide is the indicator of choice in the calcium titration the color change is from wine red to purple when the end point is reached.

Mordant black 11 triturate (also called Eriochrome black T) is the indicator of choice in the magnesium titration, the color change is from violet to deep blue.

Procedure:

(a)   Calcium carbonate

1. Transfer 10 ml of Water in C.F., dilute to 50mL with D.W.
2. Add 2mL of approximately 10 $mol.L^{-1}$ sodium hydroxide solution [CORROSIVE] and about 15 mg of Murexide indicator. Titrate with 0.1 $mol.L^{-1}$ sodium edentate until the color changes from wine red to purple.

(b) Magnesium carbonate

3. Transfer 10 ml of Water in C.F., dilute to 50mL with D.W.
4. Add 2mL of ammonia buffer pH 10.0 and about 50 mg of mordant black 11 triturate.
5. Heat to 40ºC and titrate at this temperature with 0.1 $mol.L^{-1}$ disodium edentate until the color changes from violet to full blue.

Calculations:

<div align="center">

$(M \times V)_{EDTA} = (M \times V)_{CaCO_3 \text{ or } MgCO_3}$
</div>

Calculate ppm of water hardness?