CHAPTER-2

2. Principles and application of analytical techniques

OUTLINE:

- **2. Principles and application of analytical techniques:**

2.1.Gravimetry

2.2.Titrimetry

2.3.Spectroscopy

2.4.Chromatography

INTRODUCTION

Objectives:

- The end of the chapter students will explain principle & application of gravimetry, titrimetry, spectroscopy and chromatography.

❑2.1. GRAVIMETRY:

- Gravimetry is applied to samples where a good precipitating agent is available.
- The precipitate should be quantitative, easily washed and filtered and a suitable quantity for accurate weighing.
- In this technique, the analyte is converted to an insoluble form which can then be washed, dried, and weighed in order to determine the concentration of the analyte in the original solution.

CONT'D…

- Therefore, Gravimetry is regarded as a macro analytical technique.
- However, it is considered, when appropriately done, one of the most accurate analytical techniques.
- Also, Gravimetry is one of a few analytical methods that do not require standard solutions as the weight of precipitate is the only important parameter in analyte determination.

❑PRINCIPLE:

- It is process to isolating and weighting an pure compound from the solution.
- The separation of the element or the compound by following ways:

1. Precipitation methods
2. Volatilization-ignition or drying
3. Electro gravimetry

ACTIVITY -1

- What are the **Properties of Precipitates?**

- **4min.**

❑PROPERTIES OF PRECIPITATES ARE:

1. Low solubility

- No significant loss of the analyte occurs during filtration and washing

2. High purity

3. Known composition

- After drying and ignition, known chemical composition

4. Easy to separate from reaction mixture

5. Stable under atmospheric conditions

CONT'D…

Species analyzed	Precipitated form	Form weighed	Some interfering species
K^+	$KB(C_6H_5)_4$ (Potassium tetraphenylborate)	same	NH_4^+, Ag^+, Hg^{2+}, Tl^+, Rb^+, Cs^+
Mg^{2+}	$Mg(NH_4)PO_4.6H_2O$(Magnesium Ammonium Phosphate Hexahydrate)	$Mg_2P_2O_7$	Many metals except Na^+ and K^+
Ca^{2+}	$CaC_2O_4.H_2O$	$CaCO_3$ or CaO	Many metals except Mg^{2+}, Na^+, or K^+
Ba^{2+}	$BaSO_4$	$BaSO_4$ or BaS	Ca^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Sr^{2+}, Pb^{2+}
Cr^{3+}	$PbCrO_4$	same	Ag^+, NH_4^+
Mn^{2+}	$Mn(NH_4)PO_4.H_2O$	$Mn_2P_2O_7$ (Manganese pyrophosphate)	Many metals
Ni^{2+}	$Ni(dimethylglyoximate)_2$	same	Pd^{2+}, Pt^{2+}, Bi^{3+}, Au^{3+}

❑STEPS IN A GRAVIMETRIC ANALYSIS:

- After appropriate dissolution of the sample, the following steps should be followed for a successful gravimetric procedure:

1. **Preparation of the solution:** This may involve several steps including adjustment of the pH of the solution in order for the precipitate to occur quantitatively and get a precipitate of desired properties, removing interferences, adjusting the volume of the sample to suit the amount of precipitating agent to be added.

CONT'D…

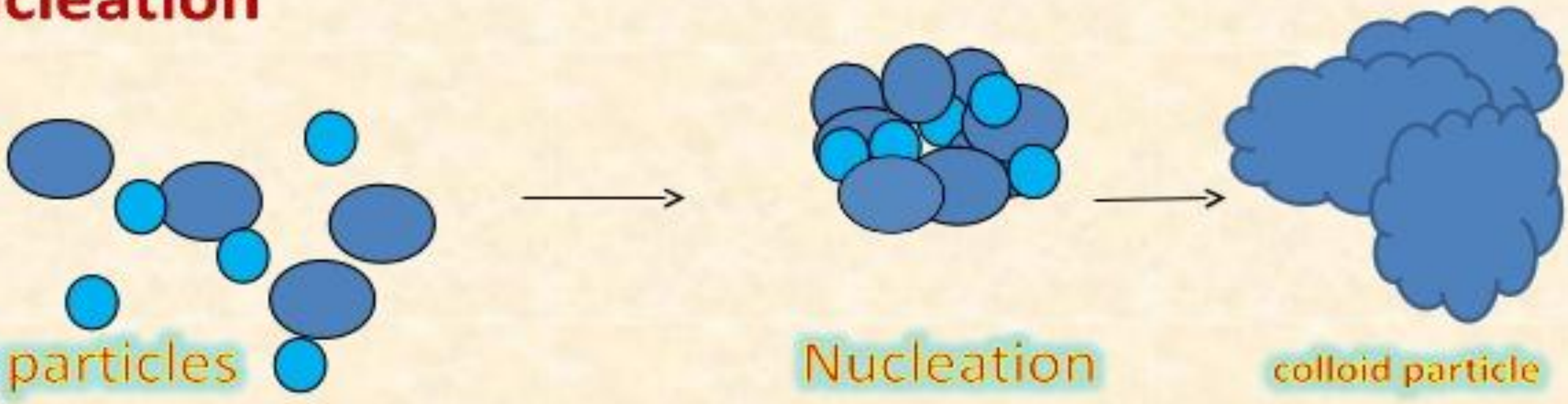
2. Precipitation:

- This requires addition of a precipitating agent solution to the sample solution.
- Addition of the first drops of the precipitating agent, super saturation occurs, and then nucleation starts to occur where every few molecules of precipitate aggregate together forming a nucleous.
- At this point, addition of extra precipitating agent will either form new nuclei or will build up on existing nuclei to give a precipitate.

CONT'D….

Nucleation- Individual ions/atoms/molecules coalescence to form "nuclei (small particles come together to form colloid particles)

❖Nucleation



Nucleation increases –

leads to more number of smaller size colloid form of crystal

Leads to adsorbs the impurity

CONT'D…

- This can be predicted by Von Weimarn ratio where, according to this relation the particle size is inversely proportional to a quantity called the relative super saturation
- Relative Super saturation = $(Q - S)/S$
- where:
- Q- is the concentration of reactants before precipitation,
- S- is the solubility of precipitate in the medium from which it is being precipitated.
- Therefore, in order to get particle growth instead of further nucleation we need to make the relative super saturation ratio as small as possible.

CONT'D…

- **The optimum conditions for precipitation which make the super saturation low are:**

1. Precipitation using dilute solutions to decrease quantity
2. Slow addition of precipitating agent to keep Q as low as possible
3. Stirring the solution during addition of precipitating agent to avoid concentration sites and keep Q low
4. Increase solubility by precipitation from hot solution
5. Adjust the pH in order to increase S but not a too much increase as we do not want to lose precipitate by dissolution
6. Usually add a little excess of the precipitating agent for quantitative precipitation and check for completeness of the precipitation.

CONT'D…

7. Precipitation from Homogeneous Solution:

- ✓ In order to make Q minimum we can, in some situations, generate the precipitating agent in the precipitation medium rather then adding it.
- ✓ For example, in order to precipitate iron as the hydroxide, we dissolve urea in the sample.
- ✓ Heating of the solution generates hydroxide ions from the hydrolysis of urea.
- ✓ Hydroxide ions are generated at all points in solution and thus there are no sites of concentration.
- ✓ We can also adjust the rate of urea hydrolysis and thus control the hydroxide generation rate. This type of procedure can be very advantageous in case of colloidal precipitates.

CONT'D…

- **3. Digestion of the Precipitate:**

✓ The precipitate is left hot (below boiling) for 30 min to 1 hour in order for the particles to be digested.

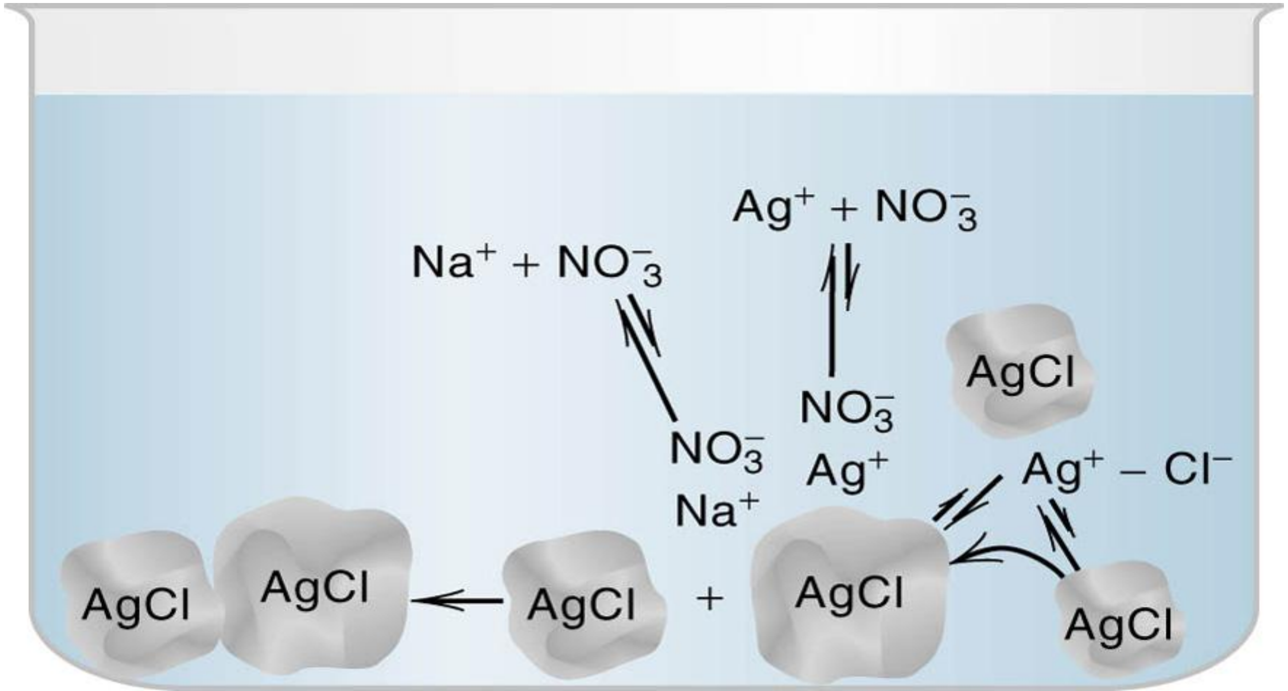
✓ Digestion involves dissolution of small particles and reprecipitation on larger ones resulting in particle growth and better precipitate characteristics.

✓ Digestion forces the small colloidal particles to agglomerate which decreases their surface area and thus adsorption.

CONT'D…

- **During digestion at elevated temperature:**

1. Small particles tend to dissolve and reprecipitate on larger ones.
2. Individual particles agglomerate.
3. Adsorbed impurities tend to go into solution.



CONT'D…

- **4. Filtering and Washing the Precipitate:**

- It is crucial to wash the precipitate very well in order to remove all adsorbed species which will add to weight of precipitate.
- One should be careful not to use too much water since part of the precipitate may be lost.
- Also, in case of colloidal precipitates we should not use water as a washing solution since peptization would occur.
- In such situations dilute nitric acid, ammonium nitrate, or dilute acetic acid may be used. Usually, coagulated particles return to the colloidal state if washed with water, a process called peptization.

CONT'D…

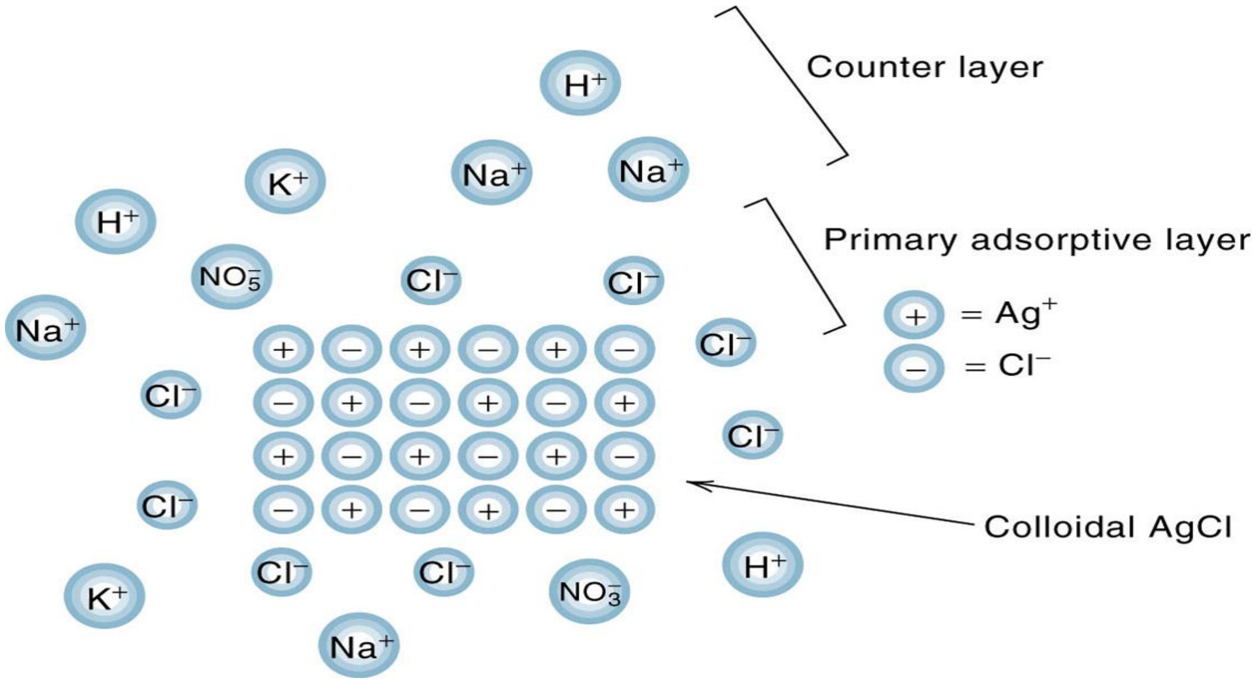
- **Washing of Precipitates**

$$\text{Colloid} \underset{\text{Peptization}}{\overset{\text{Agglomeration}}{\rightleftharpoons}} \text{Precipitate}$$

❑ADSORPTION AND PARTICLE SIZE:

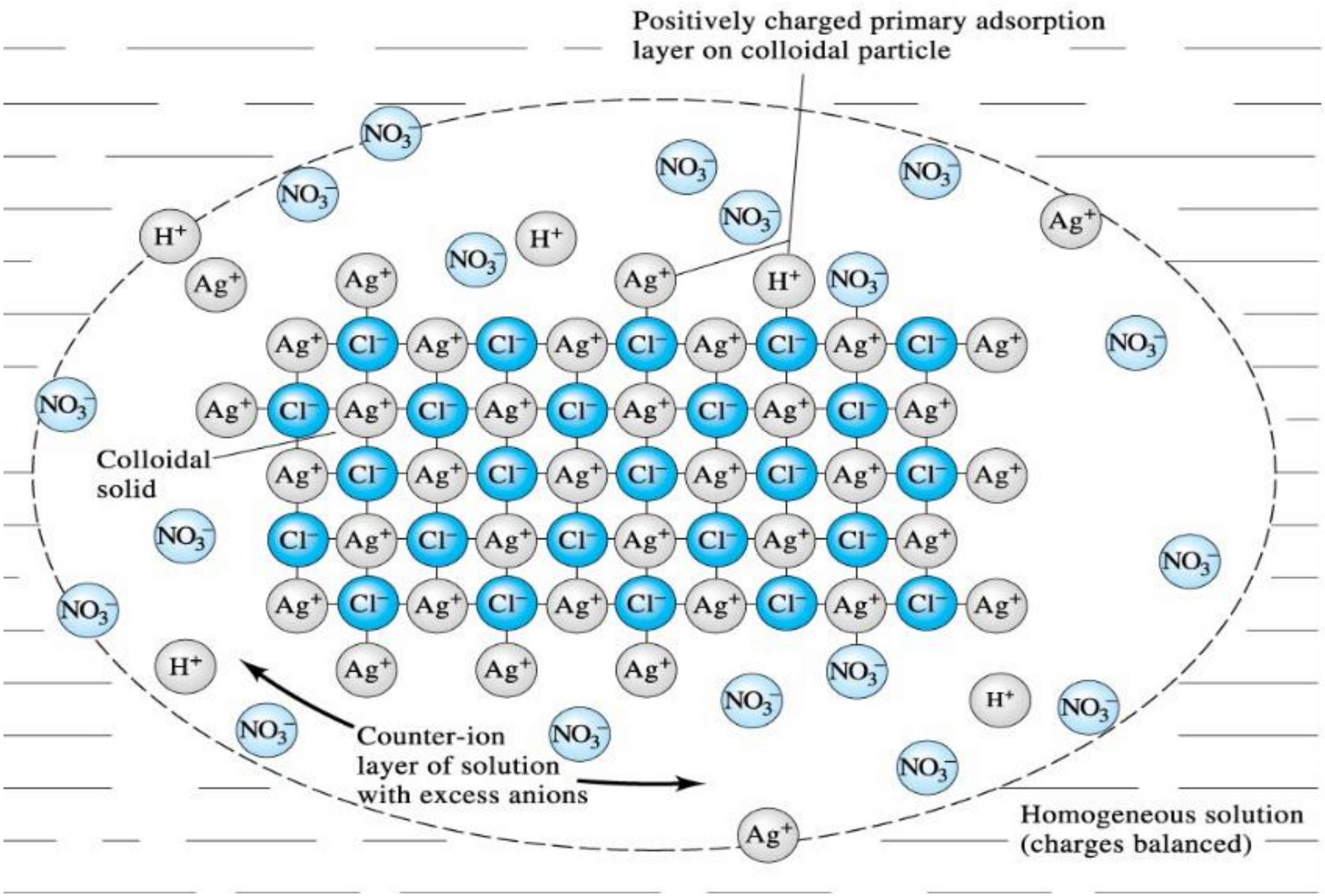
- You should know that adsorption is a major problem in gravimetry in case of colloidal precipitate since a precipitate tends to adsorb its own ions present in excess, forming what is called a primary ion layer which attracts ions from solution forming a secondary or a counter ion layer.
- Individual particles repel each other keeping the colloidal properties of the precipitate.
- Particle coagulation can be forced by either digestion or addition of a high concentration of a diverse ions strong electrolytic solution in order to shield the charges on colloidal particles and force agglomeration.

CONT'D…



Representation of silver chloride colloidal particle and adsorptive layers when Cl^- is in excess.

CONT'D….


Positively charged primary adsorption layer on colloidal particle
Colloidal solid
Counter-ion layer of solution with excess anions
Homogeneous solution (charges balanced)
Ag^+
Cl^-
NO_3^-
H^+

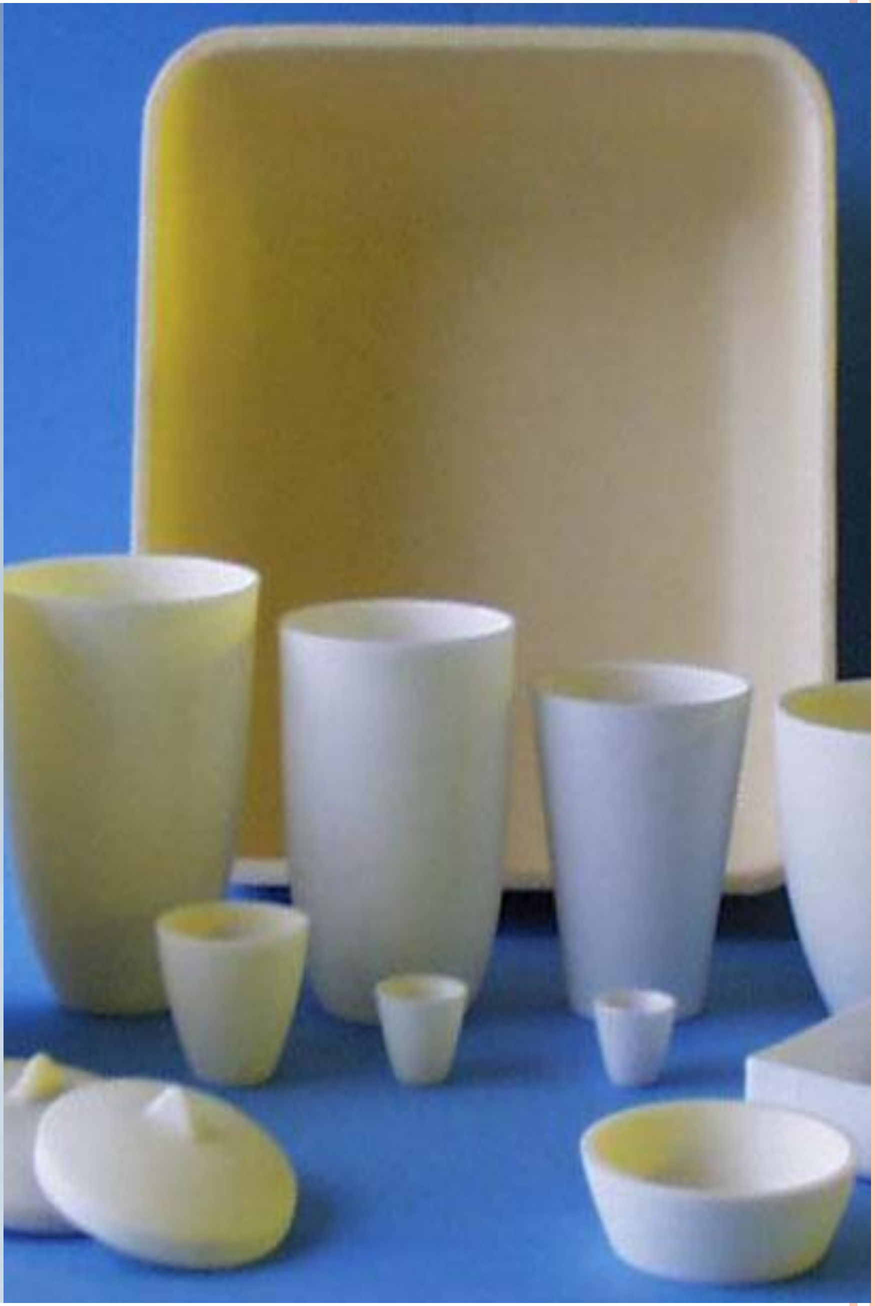
CONT'D…

- Cl^- or Ag^+ adsorbs on the particles when in excess (primary ion layer).
- A counter layer of cations forms.
- Washing with water will dilute the counter ion layer and the primary layer charge causes the particles to revert to the colloidal state (peptization).
- So we wash with an electrolyte that can be volatilized on heating (HNO_3).

CONT'D…

- **5. Drying and Ignition:**
- The purpose of drying (heating at about 120-150 ^{o}C in an oven) or ignition in a muffle furnace at temperatures ranging from 600-1200 ^{o}C is to get a material with exactly known chemical structure so that the amount of analyte can be accurately determined.

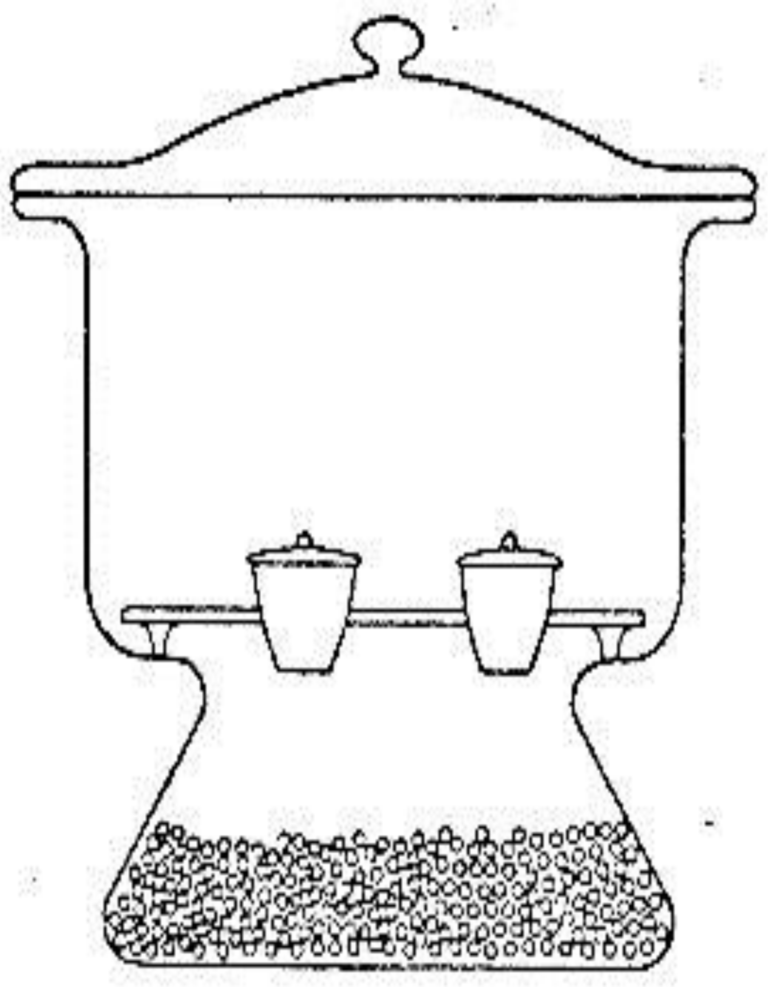

PYREX
ENGLAND
2
PYREX
ENGLAND
3



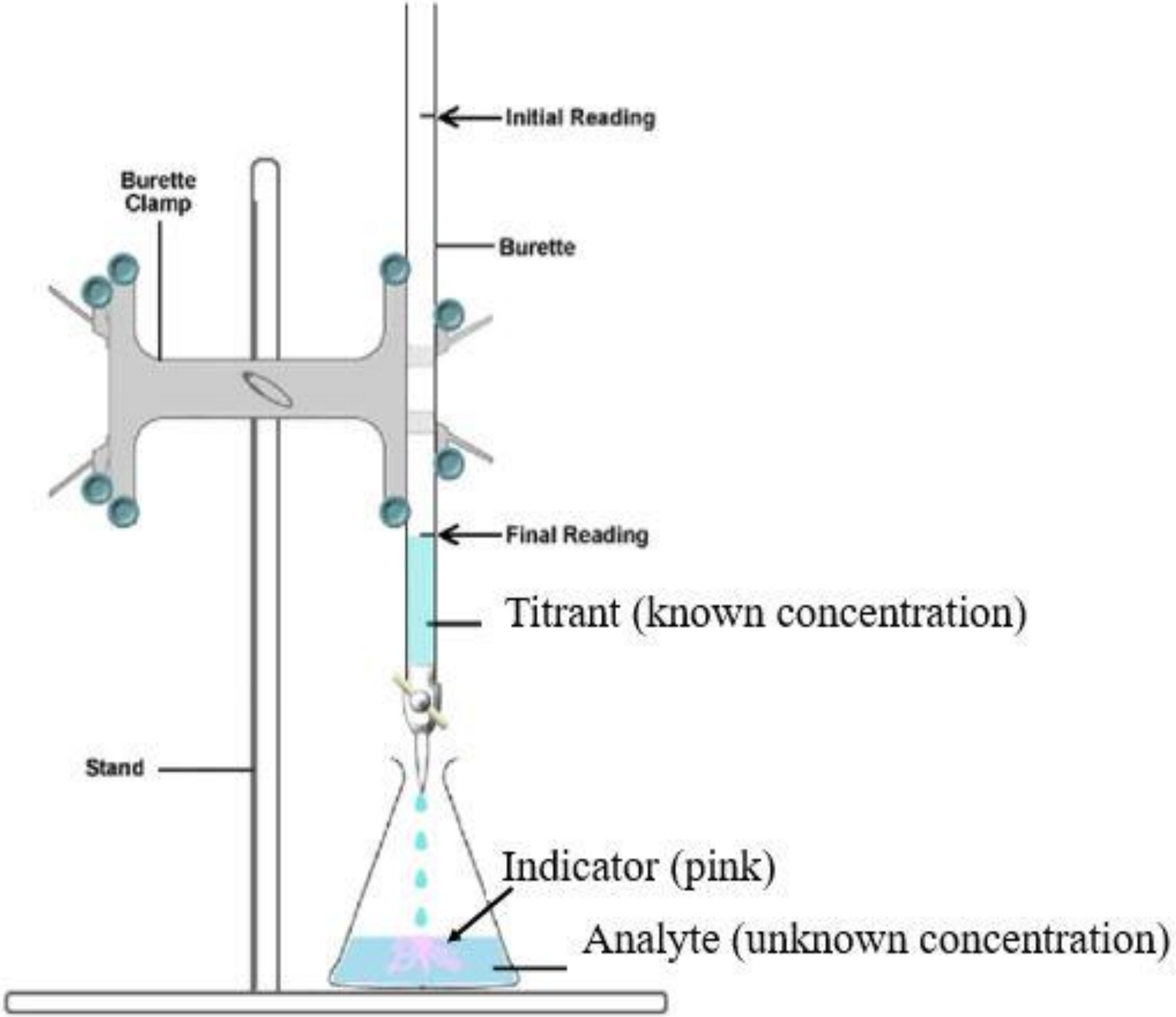
CONT'D…


Vacuum Oven
Drain Tap
Power
Vacuum
OPEN
OFF
SHANGHAI SHENXIAN THERMOSTATIC
EQUIPMENT FACTORY


1400
Furnace
106



2.2.Titrimetry



❑TITRIMETRY:

- Titration: A process in which a standard reagent is added to a solution of an analyte until the reaction between the analyte and reagent is judged to be complete.
- Standard solution: A reagent of exactly known concentration that used in a titrimetric analysis.
- Back –titration: a process in which the excess of a standard solution used to consume an analyte is determined by titration with a second standard solution.

PURPOSE OF BACK TITRATION:

- Back titration is designed to resolve some of the problems encountered with forward or direct titration.
- The possible reasons for devising back titration technique are:

1. The analyte may be in solid from
2. The analyte may contain impurities which may interfere with direct titration.
3. the analyte reacts slowly with titrant in director forward titration.
4. weak acid –weak base reactions can be subjected to back titration for analysis of solution of unknown concentration.

CONT'D…

- Equivalence points and end points:

- Equivalence points: the point in a titration when the amount of added standard reagent is exactly equivalent to the amount of analyte.
- End point: the point in a titration when a physical change occurs that is associated with the condition of the chemical equivalence.
- Indicators: are often added to the analyte solution to produced an observable physical change at or near the equivalence point.

❑INDICATORS:

- Physical change:

✓ The appearance or disappearance of a color

✓ The change in color

✓ The appearance or disappearance of turbidity

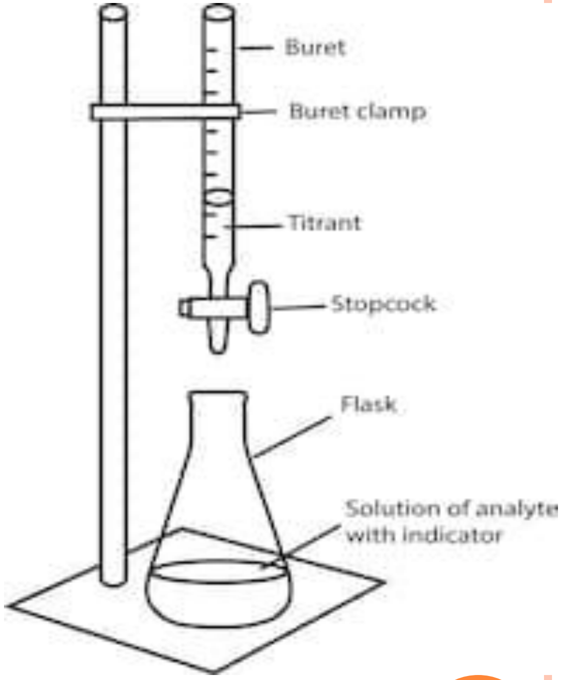
ACTIVITY

- What are the apparatus consists of titration set up?

4min.

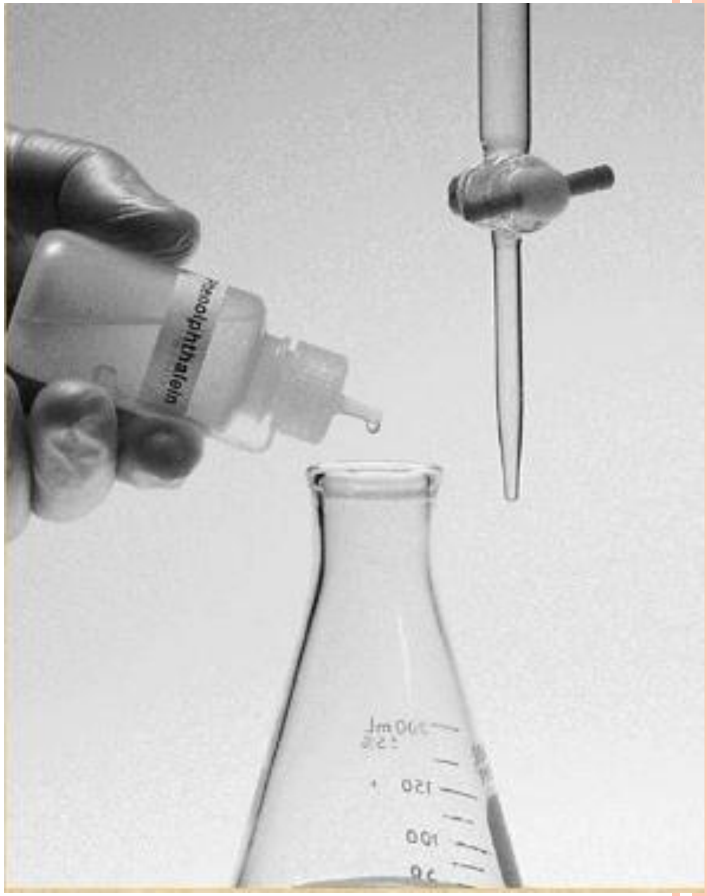
CONT'D…

- Typical setup for carrying out a titration.
- The apparatus consists of:
- a buret,
- buret stand and clamp and
- a wide-mouth flask containing a precisely known volume of the solution to be titrated.
- The solution is normally delivered into the flask using a pipet, as shown in.



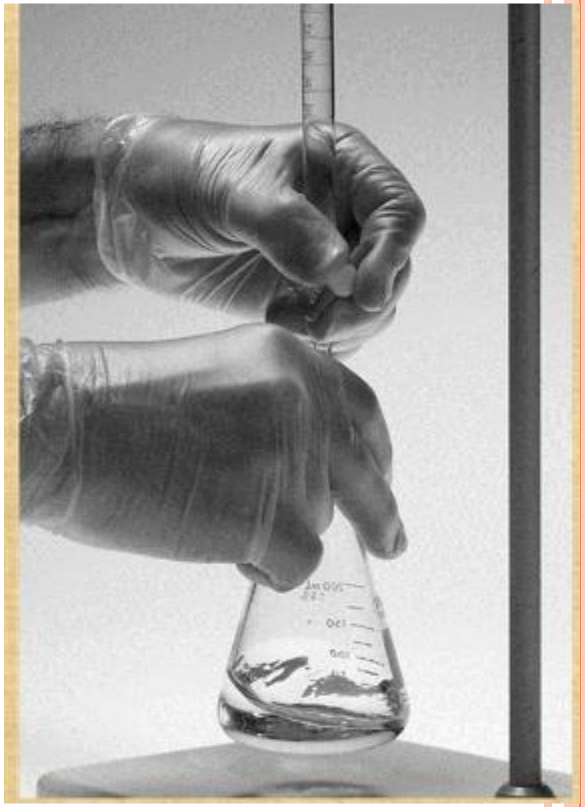
CONT'D…

- The solution to be titrated, an acid in this example, is placed in the flask and the indicator is the flask and the indicator is added as shown in the photo.
- The indicator in this case is phenolphthalein, which turns pink in basic solution.



CONT'D…

- The titrant is added to the flask with move quickly until the color of the indicator persists.
- In the initial region of the titration,titrant may be added rather rapidly, but as the end point is approached, increasingly smaller portions are added at the end point ,less than half a drop of titrant should cause the indicator to change color.



- 2.3.Spectroscopy

❑ INTRODUCTION:

- **Spectroscopy :**

- It is the branch of science that deals with the study of interaction of matter with light.

or

✓ It is the study of interaction of electromagnetic radiation with matter as a function of wavelength.

❑PRINCIPLES OF SPECTROSCOPY:

- The principle is based on the measurement of spectrum of a sample containing atom/molecules.
- Spectrum is a graph of intensity of absorbed or emitted radiation by sample verses frequency(V) or wavelength.

CONT'D….

- Spectroscopy is often used in physical and analytical chemistry for the identification of substances through the spectrum emitted from or absorbed by them.
- Most large telescopes have spectrometers, which are used either to measure the chemical composition and physical properties of astronomical objects or to measure their velocities from the doppler shift of their spectral lines.

❑CLASSIFICATION OF METHODS:

- The type of spectroscopy depends on:

✓ the physical quality measured,

✓ the quality that measured is an intensity, either of energy absorbed or produced.

- Most spectroscopic methods are differentiated as either atomic or molecular based on whether or not they apply to atoms or molecules.

CONT'D…

- **Spectroscopy can be classified on the nature of their interaction:**

1. Absorption Spectroscopy:

- ✓ It uses the range of the electromagnetic spectra in which a substance absorbs.
- ✓ This includes atomic absorption spectroscopy and various molecular techniques, such as infra-red spectroscopy in that region and nuclear magnetic resonance spectroscopy in the radio region.

2. Emission Spectroscopy:

- ✓ It uses the range of electromagnetic spectra in which a substance radiates(emits).
- ✓ The substance first must absorb energy. This energy can be from a variety of sources, which determines the name of the subsequent emission, like luminescence.

CONT'D…

3. Scattering spectroscopy:

- ✓ It measures the amount of light that a substance scatters at certain wavelengths, incident angles, and polarization angles.
- ✓ The scattering process is much faster than the absorption/emission process.
- ✓ One of the most useful applications of light scattering spectroscopy is raman spectroscopy.

❑COMMON TYPES OF SPECTROSCOPY ARE :

- ✓ Fluorescence spectroscopy
- ✓ X-ray spectroscopy
- ✓ Flame spectroscopy:
    - 1-Atomic emission spectroscopy
    - 2-Atomic absorption spectroscopy
    - 3-Atomic fluorescence spectroscopy
- ✓ Plasma emission spectroscopy
- ✓ UV-spectroscopy
- ✓ IR-spectroscopy
- ✓ Photo thermal spectroscopy
- ✓ Thermal infra-red spectroscopy
- ✓ Mass spectroscopy

1.X-RAYS SPECTROSCOPY:

- X-rays of sufficient frequencies interact with material and excite the atoms contained.
- X-rays absorption and emission spectroscopy is used in chemistry and material sciences to determine elemental composition and chemical bonding.

2.FLAME SPECTROSCOPY:

- Liquid solution samples are aspirated into a burner or nebulizer combination, desolvated, atomized, and sometimes excited to a higher energy electronic state.
- The use of a flame during analysis requires fuel and oxidant, typically in the form of gases.
- Common fuel gases used are acetylene(ethylene)or hydrogen.
- Common oxidant gases used are oxygen, air, or nitrous oxide.

CONT'D….

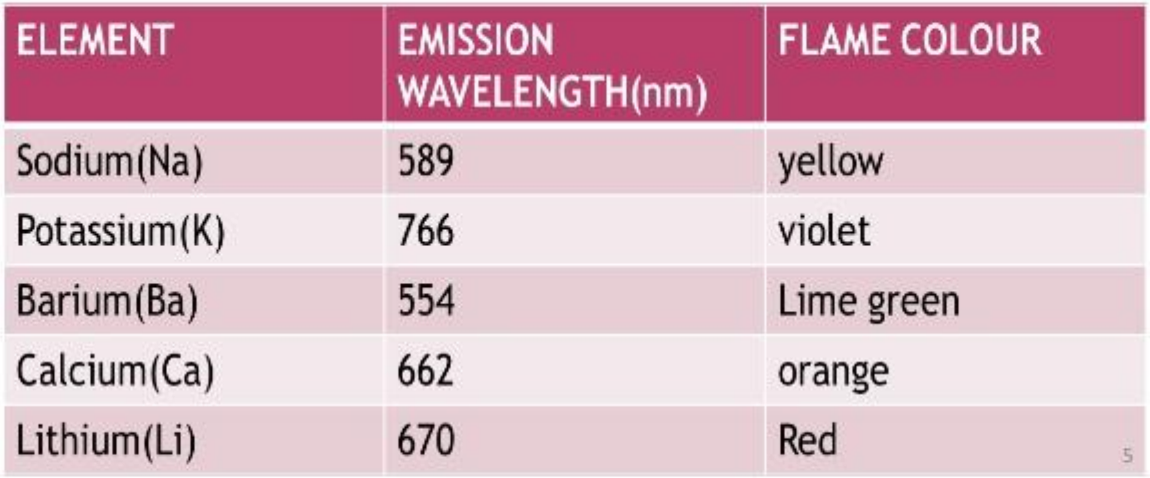
- Flame spectroscopy: is an instrument used in inorganic chemical analysis to determine the concentration of certain metal ions among them sodium, potassium, calcium and lithium.
- Flame spectroscopy: is based on measurement of intensity of the light emitted when a metal is introduced into flame.

  - the wavelength of colour tells what the element is (qualitative)

  - the colour's intensity tells us how much of the element present(quantitative).

CONT'D…

- The basic principle upon which atomic spectroscopy works is based on the fact that" Matter absorbs light at the same wavelength at which it emits light".
- When a metal salt solution is burned, the metal provides a colored flame and each metal ion gives a different colored flame.



ELEMENT	EMISSION WAVELENGTH(nm)	FLAME COLOUR
Sodium(Na)	589	yellow
Potassium(K)	766	violet
Barium(Ba)	554	Lime green
Calcium(Ca)	662	orange
Lithium(Li)	670	Red

3.UV-SPECTROSCOPY:

- ✓ It basically involves the spectroscopy of photons and spectrophotometery.
- ✓ It uses light in the visible and adjacent near ultraviolet (UV) and near infrared ranges.
- ✓ UV-spectroscopy is routinely used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds.

CONT'D…

- Ultraviolet spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface.
- UV-spectroscopy is concerned with the study of absorption of uv radiation which ranges from 200-400nm.

4.INFRA-RED SPECTROSCOPY:

- It is the subset of spectroscopy that deals with the infrared region of the electromagnetic spectrum.
- It covers a range of techniques, the most common being a form of absorption spectroscopy.
- As with all spectroscopic techniques, it can be used to identify compounds or investigate sample composition.
- Infrared spectroscopy offers the possibility to measure different types of inter atomic bond vibrations at different frequencies.
- Especially in organic chemistry the analysis of IR absorption spectra shows what type of bonds present in the sample.

CONT'D…

- IR-spectroscopy is the study of absorption of infrared radiation which results in vibration transitions.
- It is useful tool to identify functional groups in organic molecules

5. nuclear magnetic resonance:

- It is a phenomenon which occurs when the nuclei of certain atoms are immersed in a static magnetic field and exposed to an oscillating electromagnetic field.
- Nuclear magnetic resonance spectroscopy analysis the magnetic properties of certain atomic nuclei to determine different electronic local environments of hydrogen, carbon, or other atoms in an organic compound or other compound.
- This is used to help determine the structure of the compound.

CONT'D…

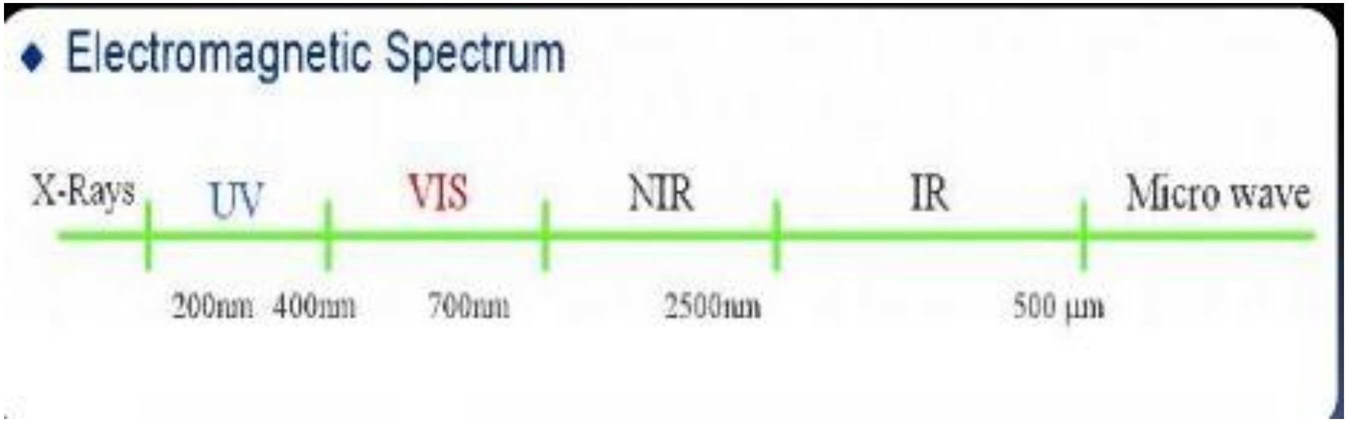
- Nuclear magnetic resonance spectroscopy is the used to study :
  - -physical properties of matter,
  - -chemical properties of matter and
  - - biological properties of matter.

CONT'D…

- 5.photo thermal spectroscopy:
- It is a group of high sensitivity spectroscopy techniques used to measure optical absorption and thermal characteristics of a sample.
- The basis of photo-thermal spectroscopy is the change in thermal state of the sample resulting from the absorption of radiation.
- Light absorbed and not lost by emission results in heating.
- The heat raises temperature thereby influencing the sample thermodynamic properties.
- Measurement of the temperature, pressure, and density changes that occur due to optical absorption are ultimately the basis for the photo-thermal spectroscopic measurements.

6. SPECTROPHOTOMETER:

- Light source are:
- To provide a sufficient of light which is suitable for making a measurement.
- ✓ Tungsten lamp
- ✓ Hydrogen lamp
- ✓ Xenon lamp



I.TUNGSTEN LAMP:

- It is the most common light source used in spectrophotometer wavelength range of about 330 to 900nm
- It has long life about 1200h

II. HYDROGEN LAMPS:

- For the ultraviolet region, hydrogen lamps are frequently used.
- Their range is approximately 200 to 450nm.

III.XENON FLASH LAMPS:

- Xenon flash lamps have several advantages as the following:

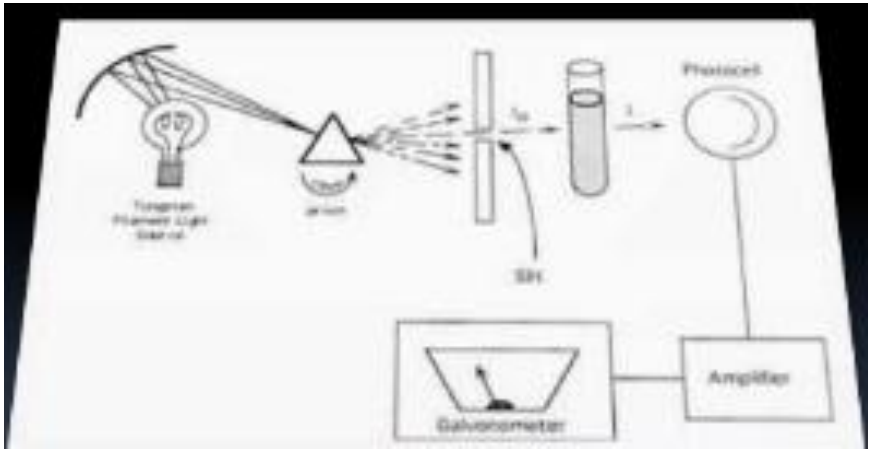
1. .The range between(190nm-1000nm)
2. Emit both UV and visible wavelengths
3. Long life
4. Do not heat up the instrument
5. Reduce warm up time

❑DISPERSION DEVICES:

- Dispersion devices causes a different wavelength of light to be dispersion at different angles.

❑ Types of dispersion devices used are:

1. **Prism**: it is used to isolate different wavelength prism may be made of glass or quartz.



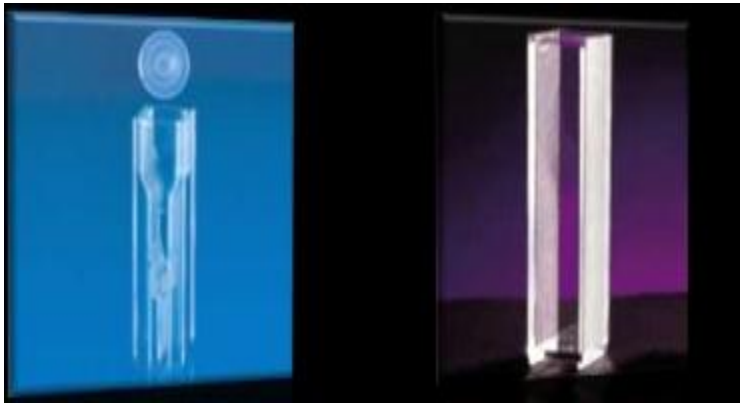
2. FILTERS:

- Filters separate different parts of the electromagnetic spectrum by absorbing or reflecting certain wavelengths and transmitting other wavelengths.
- Absorption filters are glass substrates containing absorbing species that absorb certain wavelength.
- A typical example is a cut on color filiter, which blocks short
- Wave lengh light, and transmits longer wavelength.

❑ABSORPTION CELL(CUVETTES)

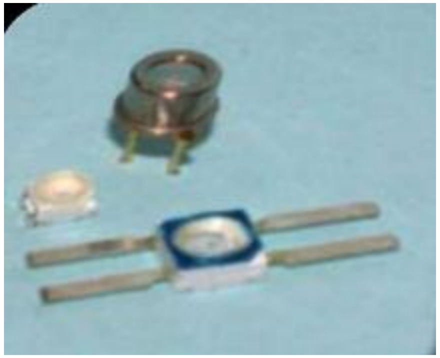
- A cuvette is a kind of cell (usually a small square tube) sealed at one end,
- It made of plastic, glass or optical grade quartz and

It is designed to hold samples for spectroscopic experiments.



❖ DETECTORS:

- Any photosensitive device can be used as a detector of radiant energy.
- The photocell and phototube are the simplest photo detectors, producing current proportion to the intensity of the light striking them.



❑DISPLAY DEVICES:

- The data from a detector are displayed by a readout device, such as :

- ✓ an analog meter,
- ✓ a light beam reflected on a scale, or
- ✓ a digital display, or liquid crystal display.
- The output can also be transmitted to a computer.

❑USES OF SPECTROPHOTOMETER:

- To determines the absorbance or transmission of characteristic wavelengths of radiant energy(light) by a chemical species in solution.
- Identify organic compounds by determining the absorption maximum.
- Used for color determination within the spectral range

ACTIVITY

- Summarized

Thank you!!!