

# I. Introduction to Characterization techniques

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## Introduction to instrumental methods of Characterization:

Characterization techniques are concerned with the identification of the substance, elucidation of its structure and quantitative analysis of its composition.

Instrumental methods are those which measure an electrical property, absorption of radiation, or the intensity of an emission using a suitable instrument.

## Advantages of instrumental methods of characterization

1. Very small concentrations can be estimated very accurately which is not possible in chemical methods.
2. Determination procedure is simpler & faster compared to chemical methods.
3. Complex samples can be handled easily & efficiently.
4. Measurements obtained are reliable & accurate
5. Microcomputers can be interfaced to the instrument so that absorption curves, polarograms, Spectral patterns etc can be plotted automatically.

## Limitations of instrumental methods.

1. There is a requirement for calibration curve / operation using a sample of material of known composition as ref. substance.
2. Many instruments are expensive
3. Specialized training is needed.

## Classification of characterization techniques

Characterization techniques are classified into

1. Classical Methods & (2) Instrumental methods
1. Classical Methods are further classified into (a) Gravimetry  
(b) Titrimetry.

Gravimetric Analysis: Here the substance being determined is converted into insoluble ppt which is collected and weighed.

Electrogravimetry: Here electrolysis is carried out and the material is deposited on one of the electrodes is weighed.

Thermal Gravimetry: Records the changes in the weight of the substance as a function of temperature.

Differential Thermal Analysis: Records the difference in temp<sup>(DTA)</sup> between a test substance and an inert reference material.

Differential Scanning Calorimetry (DSC): Records the energy required to establish a zero temperature difference between a test-substance and a reference material.

2. Titrimetry/Volumetry: The analyte is allowed to react with an appropriate a std. soln. and the volume of the soln needed for complete reaction is determined.

### Classification of instrumental methods of analysis

I. Electroanalytical Methods: These methods involve the measurement of current, voltage or resistance with respect to concn of a certain species in solution.

Eg: ① Electrogravimetry - Electrolysis is carried out and the material deposited on one of the electrode is weighed.

② Cathometry - Deposition of matter on an electrode by electrolysis. Quantity of electricity and time is measured.

③ Conductometry - Change in electrical conductivity of a solution in a chemical reaction. Conductivity/ resistivity is measured.

④ Amperometry - Potential applied between the indicator electrode and depolarized ref. electrode is kept constant, current is measured.

⑤ Potentiometry - Change in electrode potentials of a system during chemical reaction & ~~the~~ <sup>the</sup> potential is measured.

⑥ Polarography - Electrode is polarized and the current is measured as a fun of applied Voltage.

II Spectroscopic Methods: Interaction of matter with <sup>(3)</sup> electromagnetic radiation, radiant energy of a particular wavelength is measured.

- Eg:
- ① Atomic absorption spectroscopy: Absorption of radiation is measured by atomising the Specimen.
  - ② Absorption spectrophotometry: Absorption of radiant energy by molecules - UV & visible spectroscopy.
  - ③ IR spectroscopy: Absorption of IR radiation due to molecular vibrations
  - ④ NMR / ESR: Absorption of radio frequency wave due to spin energy changes in the molecule
  - ⑤ Mass Spectroscopy: Ionization of atoms, ions and molecules by a combined action of electric & magnetic fields.
  - ⑥ X-ray Spectroscopy: By analysing position & intensity of spectral lines information about can be obtained.

III X-ray Diffraction Technique: Diffraction of X-ray by atoms, to give information about the crystal str. of the Compd.  
Basic Components involved in instrumental methods of Characterization :

(i) generation of a signal The basic components are



(1) Energy Source : Required for the generation of signal which will interact with the analyte sample.

(2) Analyte (Sample) compartment: The compartment where the analyte is placed. Different samples are handled in a suitable required way. Sample interacts with the signal.

(3) Transducer: It converts original analytical signal to one that is more conveniently measured.  
Eg. photocells, photomultiplier tubes, thermocouples etc.

(4) Data processor: The data collected from the transducer is processed with the help of microprocessor/computers, amplified (electronically/mechanically).

(5) Recorder: presentation of signal is done in the recorder. The transduced and amplified signal from the is generally presented as linear or angular displacements along a scale.

### Basics of measurements

Errors: "The degree of uncertainty associated with every measurement" and one can at best decrease is called error.

Types of errors — (1) Determinate error

(2) Indeterminate error

(1) Determinate errors: Determinate errors are those that are determinable and can either be avoided or corrected.

The Determinate errors are further classified into

(i) Instrumental errors

(ii) Operative errors

(iii) Errors of the method

(i) Instrumental errors: The errors are due to limited accuracy of the instrument. Calibration of the instrument in one range may not be valid for the entire range.

(ii) Operative errors: These are personal errors and can be reduced by experience. The errors that may occur when transferring solutions, sample dissolution, incomplete drying of samples

(Methodic errors) (iii) Errors of the method: These are the most serious errors of an analyst and are inherent in the method ~~so~~ cannot be changed unless the conditions of the determination are changed. The methodic errors are coprecipitation of impurities, side reaction, slight solubility of precipitate, impurities in reagents etc.

(2) Indeterminate Errors: These are accidental or random errors which cannot be predicted or determined. These errors follow a random distribution, the law of mathematical probability can be applied to arrive at conclusion.

- Eg: Incorrect reading by an analyst  
Incorrect handling of pipettes etc

Precision: It is the variability among the replicate measurements. "precision tells about the closeness of values in each series of results under identical conditions, but for different trials." It has nothing to do with the true value.

Accuracy: It is the closeness of the observed value and to that of the true value.

Accuracy can be expressed in terms of absolute error and relative error.

Absolute error : (d): Absolute error of a measured value is a numerical difference between true value ( $\mu$ ) and the observed value ( $x$ ) i.e.,  $d = \mu - x$ . Absolute error can be +ve or -ve.

Relative error : (e): It is the absolute error divided by the true value  $e = \frac{d}{\mu} = \frac{\mu - x}{\mu} \times 1000$

problem: The result of an analysis was determined as 15.752 g while the accepted value was 15.872 g calculate the absolute & relative error.

$$\text{Solu. Absolute error} = \frac{\text{True value} - \text{observed value}}{\text{True value}} \\ = 15.872 - 15.752 = 0.120$$

$$\text{Relative error} = \frac{\text{Absolute error} \times 1000}{\text{True value}} = \frac{0.120 \times 1000}{15.872} = 7.56$$

### Minimization of errors:

1. Calibration of apparatus & corrections: Glasswares and instruments should be calibrated & appropriate corrections are applied to the original measurements. If the error cannot be eliminated, a correction factor should be applied.
2. Running a control determination: carrying out a determination for a standard substance under identical conditions as that of the unknown sample.
3. Running a blank determination: carrying out a separate determination by omitting the sample, under exactly the same exptl conditions as that of the sample.
4. Running parallel determination: conduction of the experiment in duplicates and triplicates & the parallelly. The values obtained in parallel dets<sup>n</sup>s should agree well among themselves.
5. Internal Standards: Adding a fixed amount of a reference material (Int. Std) to a series of known concns of the sample to be determined. The ratios of the values of the int. Std, to the series, to be plotted against Conc<sup>n</sup> values.
6. Standard Addition: to get a straight line
7. Standard Addition: A known amount of the constituent being determined is added to the sample, which is then analysed for the total amount of constituent present. The difference b/w the analytical results for samples wth & without the added constituent present gives the recovery of the amount of added constituent.

7. Isotopic Dilution: A known amount of an element being determined (containing a radioactive isotope) is mixed with the sample & the element is isolated in a pure form & is weighed. The radioactivity of the isolated material is measured and compared with that of the added element.

8. Amplification Methods: If the signal produced is weak in the case of very small amount of sample, it can be increased by amplification methods.

### Signals and Noise in analytical Instruments

Signal: Carries the information about the analyte.

Noise: Noise is made up of extraneous information that is unwanted because it decreases the accuracy & precision of an analysis.

Signal to Noise ratio (S/N): It is the ratio of the mean of the measurements to the standard deviation.

$$S/N = (\text{mean}) / \text{Standard deviation} = \frac{\bar{x}}{s} = \frac{1}{RSD}$$

$\bar{x}$  = mean of the measurements

s = standard deviation of measurements.

RSD = Relative standard deviation.

Sources of Noise (1) Chemical Noise  
(2) Instrumental Noise.

Chemical Noise: Chemical noise arises from uncontrollable variables that affect the chemistry of the system being analyzed.

Ex: Undetected variations in temperature, pressure, chemical eqbm, humidity, light intensity etc.

Instrumental Noise: Noise associated with each component of an instrument - i.e., with the source, the input transducers, signal processing elements and output transducer

Eg: Thermal noise, Shot noise, flicker noise, environmental noise.

Mean: It is the summation of all the values of the data divided by the total no. of values of the data.

$$\text{Mean} = \bar{x} = \frac{\sum x_i}{n} \quad x_i = \text{Summation of all the values} \\ n = \text{Total no. of values}$$

Standard deviation: It is the positive square root of the average of squared deviation taken from arithmetic mean.

$$\text{std. deviation} = \sigma = \sqrt{\frac{\sum (x - \bar{x})^2}{n}}$$

$x$  = each of the values of the data

$\bar{x}$  = The mean of  $x$ .

$n$  = No. of data points

Signal to Noise enhancement: It should be high to get a strong signal peaks.

Two methods to enhance Signal to Noise ratio.

1. Hardware:- Analog filtering, using Difference amplifiers, Modulation correction

2. Software correction- Digital filtering, Ensemble averaging, Boxcar averaging

These methods are based on bandwidth reduction and Signal averaging.

Hardware correction: Noise is reduced by incorporating the components such as filters, choppers, shields, modulators and synchronous detectors into the instrument. These components will remove or decrease the noise without affecting the analytical signal significantly. Examples mentioned above

Software correction: This is based on digital computer algorithms that permit extraction of signal from noisy environment. Examples mentioned above.

Amplifiers: Amplifiers are the devices that increase the amplitude of the input signal.

Amplifiers increase only the amplitude & other parameters such as frequency & shape remain constant.

Three categories of amplifiers.

1. Voltage amplifier & current amplifier & power amplifier.

1. Voltage amplifier: They are the most common amplifiers used in the electronic devices. These amplifiers increase the amplitude of the output voltage of the signal.

2. Current amplifiers: These amplifiers increase the amplitude of the output current compared to the input current waveform.

3. Power amplifiers: The product of the output voltage and current is increased compared to the product of input voltage and current.

Power amplifiers are further classified into based on the signal they amplify. They are:

1. Audiofrequency amplifiers (AF amplifiers)

2. Intermediate frequency amplifiers (I.F. amplifiers)

3. Radiofrequency amplifiers (RF amplifiers)

4. Ultrasonic amplifiers

5. Wide band amplifiers

6. Direct Coupled amplifiers (DC amplifiers)

7. Video amplifiers

8. Buffer amplifiers

9. Operational amplifiers (OP-Amp)

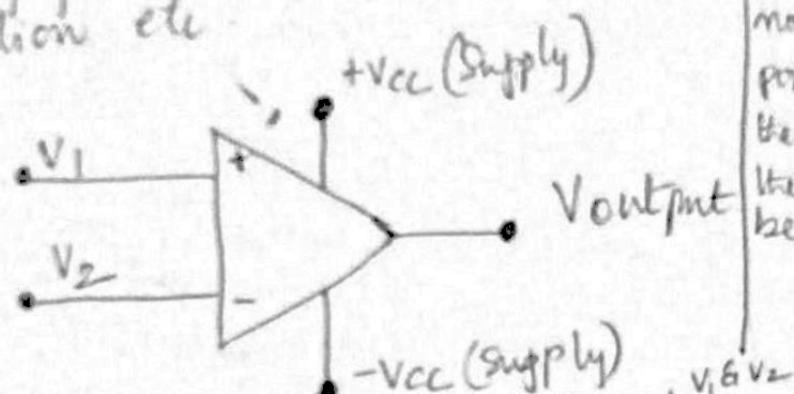
10. Transistor amplifiers

## Construction and working of operational amplifiers:

An operational amplifier is a DC coupled voltage amplifier with a very high voltage gain.

Op Amp is a multistage amplifier comprising of many transistors, FETs and resistors which are interconnected in a very complicated compact manner.

Op Amps can be configured to perform various operations like amplification, subtraction, differentiation, addition, integration etc.



Disadvantages: ① Op-Amps are mostly designed for lower power operation ② Most of the Op-Amps shut off when the load resistance is below a specific level.

An Op-Amp has two input terminals, and one output terminal. The terminal marked with -ve sign as the inverting terminal and the terminal marked with +ve sign as non inverting terminal. If we apply an input signal at the inverting (-) terminal, the output signal will be out of phase by  $180^\circ$ . If we apply signal to the noninverting terminal (+), the output signal will be in phase.

Working: Op-amp will amplify the difference between two applied input signals.

$$V_{out} = A_{OL}(V_1 - V_2)$$

$A_{OL}$  — is the open-loop gain & is constant

$V_1$  is the voltage at the non inverting terminal.  $V_2$  is the voltage at the inverting terminal.  $(V_1 - V_2)$  is the differential input voltage.

## Advantages and disadvantages of Op Amps:

- ① High open loop gain
- ② Very high input impedance
- ③ Low output impedance
- ④ High bandwidth frequency.
- ⑤ Reduced size & weight

Thermal noise: Originates from the thermally induced motions in charge carriers is known as thermal noise. Thermal agitations of es/charge carriers in resistors, capacitors, radiation detectors, cells etc.

Shot noise: Whenever es & other charged particles cross a junction like P-n, shot noises arise.

Flicker noise: It is associated with the crystal surface defects. Flicker noise decreases with frequency.

Environmental noise: It is due to a composite of noises from different sources in the environment surrounding the instrument.

# **Amplifiers**

**Amplifiers** are the devices that increase the amplitude of the input signal.

The process of increasing the signal strength is called as **Amplification**.

Almost all electronic equipment must include some means for amplifying the signals. We find the use of amplifiers in medical devices, scientific equipment, automation, military tools, communication devices, and even in household equipment.

## **Classification of Amplifiers**

### **1. Based on number of stages of Amplification**

Depending upon the number of stages of Amplification, there are Single-stage amplifiers and Multi-stage amplifiers.

- **Single-stage Amplifiers** – this has only one transistor circuit, which is a single stage amplification.
- **Multi-stage Amplifiers** – this has multiple transistor circuit, which provides multi-stage amplification.

### **2. Based on its output**

Depending upon the parameter that is amplified at the output, there are voltage and power amplifiers.

- **Voltage Amplifiers** – the amplifier circuit that increases the voltage level of the input signal, is called as Voltage amplifier.
- **Power Amplifiers** – the amplifier circuit that increases the power level of the input signal, is called as Power amplifier.

### **3. Based on the input signals**

Depending upon the magnitude of the input signal applied, they can be categorized as Small signal and large signal amplifiers.

- **Small signal Amplifiers** – When the input signal is so weak so as to produce small fluctuations in the collector current compared to its quiescent value, the amplifier is known as Small signal amplifier.
- **Large signal amplifiers** – When the fluctuations in collector current are large i.e. beyond the linear portion of the characteristics, the amplifier is known as large signal amplifier.

### **4. Based on the frequency range**

- **Depending upon the frequency range of the signals being used, there are audio and radio amplifiers.**

- **Audio Amplifiers** – The amplifier circuit that amplifies the signals that lie in the audio frequency range i.e. from 20Hz to 20 KHz frequency range, is called as audio amplifier.
- **Power Amplifiers** – The amplifier circuit that amplifies the signals that lie in a very high frequency range, is called as Power amplifier.

## 5. Based on Biasing Conditions

- Depending upon their mode of operation, there are class A, class B and class C amplifiers.
- **Class A amplifier** – The biasing conditions in class A power amplifier are such that the collector current flows for the entire AC signal applied.
- **Class B amplifier** – The biasing conditions in class B power amplifier are such that the collector current flows for half-cycle of input AC signal applied.
- **Class C amplifier** – The biasing conditions in class C power amplifier are such that the collector current flows for less than half cycle of input AC signal applied.
- **Class AB amplifier** – The class AB power amplifier is one which is created by combining both class A and class B in order to have all the advantages of both the classes and to minimize the problems they have.

## 6. Based on the Coupling method

Depending upon the method of coupling one stage to the other, there are RC coupled, Transformer coupled and direct coupled amplifier.

- **RC Coupled amplifier** – A Multi-stage amplifier circuit that is coupled to the next stage using resistor and capacitor (RC) combination can be called as a RC coupled amplifier.
- **Transformer Coupled amplifier** – A Multi-stage amplifier circuit that is coupled to the next stage, with the help of a transformer, can be called as a Transformer coupled amplifier.
- **Direct Coupled amplifier** – A Multi-stage amplifier circuit that is coupled to the next stage directly, can be called as a direct coupled amplifier.

## 7. Based on the Transistor Configuration

Depending upon the type of transistor configuration, there are CE CB and CC amplifiers.

**CE amplifier** – the amplifier circuit that is formed using a CE configured transistor combination is called as CE amplifier.

**CB amplifier** – the amplifier circuit that is formed using a CB configured transistor combination is called as CB amplifier.

**CC amplifier** – the amplifier circuit that is formed using a CC configured transistor combination is called as CC amplifier.

## **Construction and working of operational amplifiers follow from my hand written notes**

### **Calibration**

- Calibration is the act of ensuring that a scientific process or instrument will produce accurate results every time
- An instrument needs to be properly calibrated before it is used to make sure you obtain accurate results
- There are two main methods of calibration: the working curve method and the standard addition method
- An instrument needs to be calibrated after certain events, such as a knock, power-cut, or when instructed by the manufacturer

Definition: “Calibration is the activity of checking, by comparison with a standard, the accuracy of a measuring instrument”

Or

“The adjustment of the instrument to bring it into alignment with the standard”

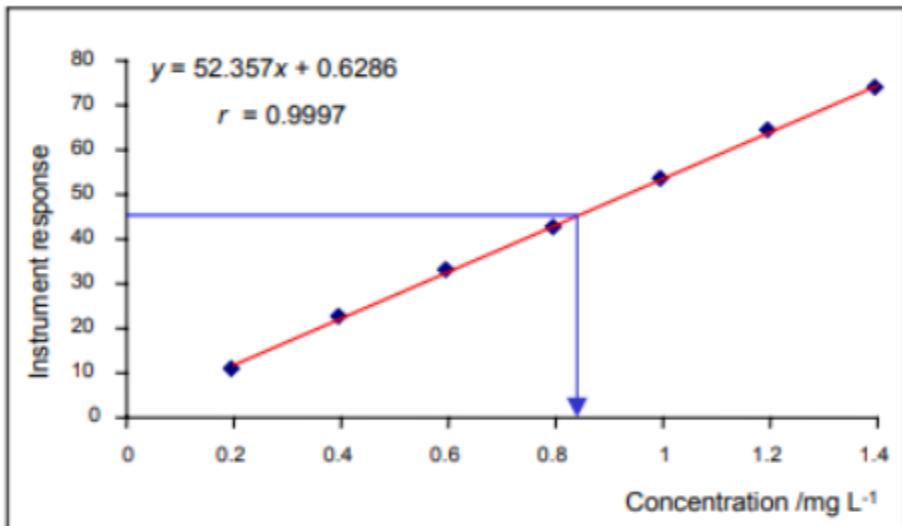
Any instrument used in research needs to be properly calibrated to make sure the data it produces is valid and can be used by others. Over time, instruments can 'drift' due to normal wear and tear and can, therefore, give inaccurate results – this is why it's important that machines are properly calibrated before use.

Any instrument used in scientific research needs to be properly calibrated before it is used – this is done through adjustment of the precision and accuracy of the instruments.

There are two main ways of calibrating an instrument – these are the calibration curve method and the standard addition method.

### **Calibration Curve method**

In the **working curve** method, a **set of standards** must be prepared. They will each contain a **known amount** of the **analyte** being measured. These standards are then measured using the instrument in question, and a **calibration curve** will be plotted. This curve will show the **relationship** between the response of the instrument and the concentration of the analyte. An example of a calibration curve can be found below.



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When using the working curve method, it is important that **each standard is prepared individually** and not all from the same stock solution. Any errors in the stock solution will carry through the entire calibration process, and thus the instrument will not be calibrated correctly.

There are a **number of steps** which should be followed when performing a **working curve** calibration, which is outlined below:

The calibration standards should **cover the range of interest** – this is so, during your actual experiment, you are sure to get the most accurate results from your curve

A ‘**blank**’ should be included in your calibration – this is a standard which contains **no analyte**

For the **standard-addition** method of calibration, two requirements must be met:

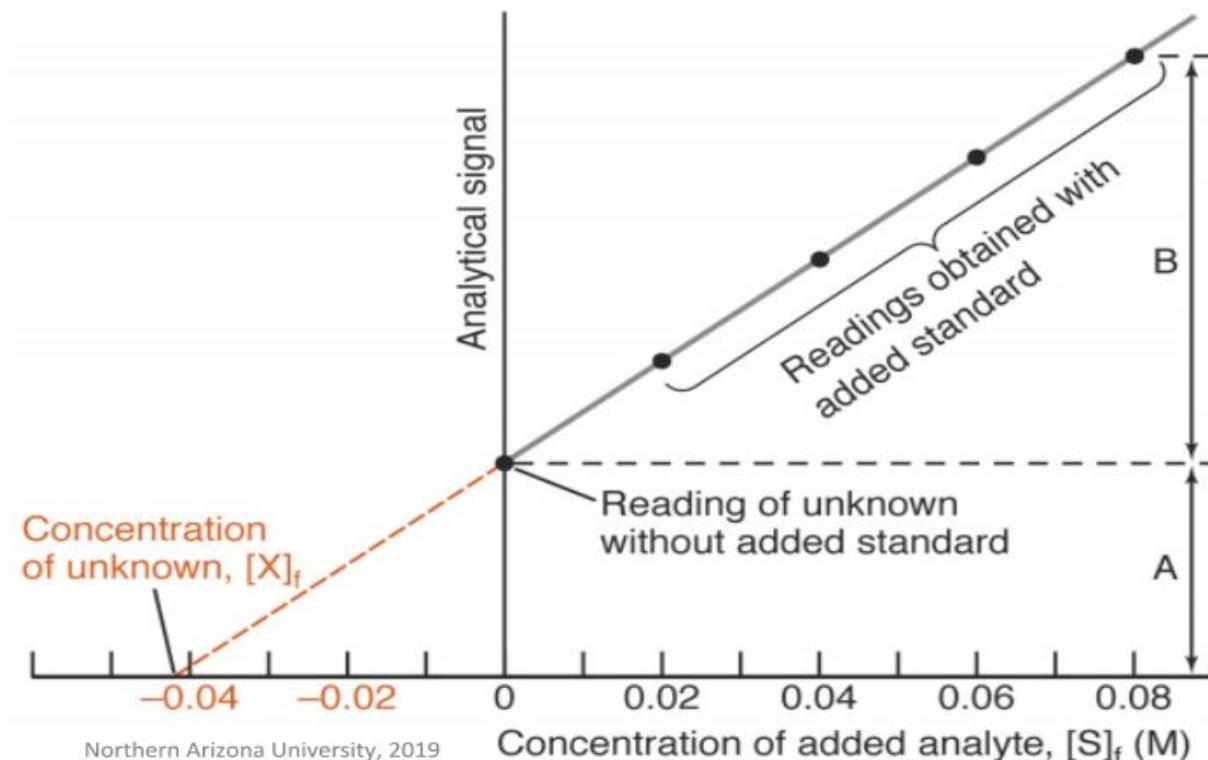
The calibration curve has to be **linear**

The regression line must **pass through zero**

In the standard addition method, the standard is added to the sample to correct for ‘matrix effects’ (a change in the analytical signal caused by anything in the sample other than the analyte). This is called “spiking.” This can be done for a single sample or for a calibration curve.

In this method, the **signal intensity** of the sample solution is measured. Then, the analyte is added to this solution at **known concentrations** – the signal intensity is measured after each addition of the analyte. This, therefore, gives a calibration curve which is **linear** and shows signal intensity vs. added concentration.

When using a calibration curve increasing amounts of analyte are added to a constant amount of sample. Then the concentration of the analyte is obtained by extrapolating back to the x-intercept; the absolute value of the x-intercept is the concentration of the unknown as shown below:



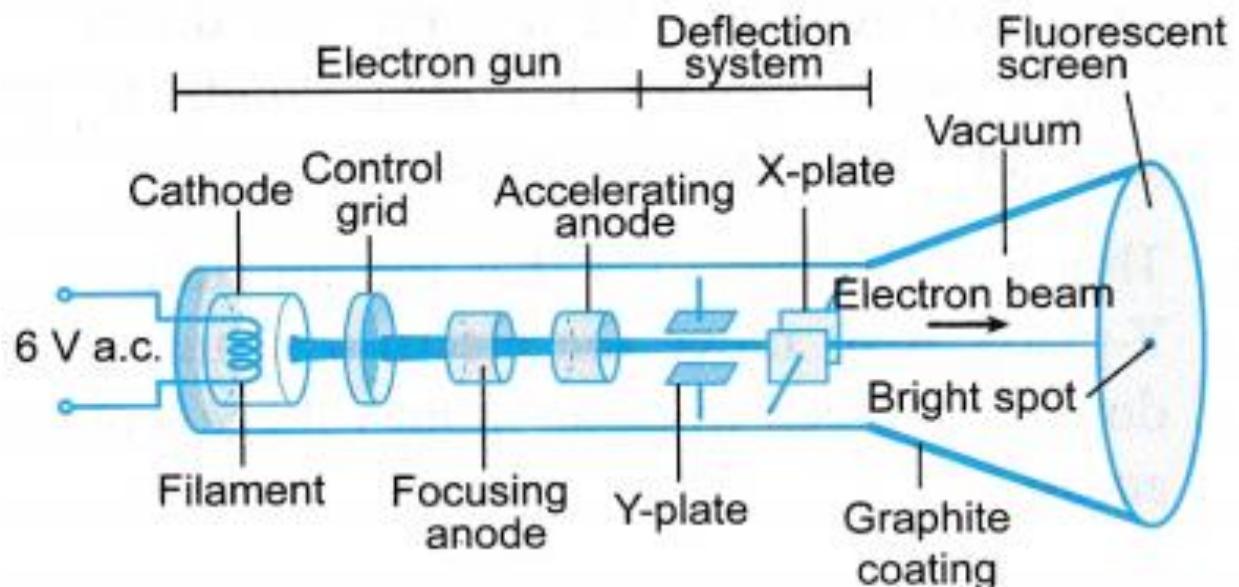
## Readout systems in analytical instruments

### Cathode Ray Tubes (CRT)

**Definition:** The CRT is a **display screen** which produces images in the form of the **video signal**. It is a type of vacuum tube which displays images when the electron beam through **electron guns** are **strikes** on the **phosphorescent surface**.

In other Words, the CRT **generates** the beams, **accelerates** it at high velocity and **deflect** it for creating the images on the **phosphorous screen** so that the beam becomes **visible**.

## Construction and working of A Cathode Ray Tube



The main parts of CRT are:-

- 1. Electron gun**
- 2. Deflection system**
- 3. Fluorescent screen**
- 4. Glass tube/envelope and base**

### 1. ELECTRON GUN

The electron gun is the source of the electron beams. The electron gun has a heater, cathode, grid, pre-accelerating anode, focusing anode and accelerating anode. The electron gun provides a sharply focused electron beam directed towards the fluorescent coated screen. The beam emitted is usually of the green colour.

### 2. DEFLECTION SYSTEM

The deflection system consists of two sets of parallel plates perpendicular to each other. One set which is arranged vertically is known as X-plates and the other set which is arranged horizontally is known as Y-plates, as shown in Figure.

The function of the Y-plates is to move the electron beam up and down the screen when an input voltage is applied across it.

The function of the X-plates is to sweep the electron beam across the screen horizontally from left to right at a steady speed.

### 3. Fluorescent Screen

1. The fluorescent screen is coated on the inside surface with some fluorescent material such as phosphor or zinc sulphide.
2. When electrons in the beam strike the screen, the material fluoresces and becomes luminous or glows. This enables a bright spot to appear wherever an electron beam strikes the screen.
3. Electrons are particles and they have mass. Since they move with high speed, they have kinetic energy.
4. When these high-energy electrons strike the screen, the fluorescent coating on the screen converts the kinetic energy of the electrons into light energy.

#### **4. Glass envelope:**

The working parts of a CRT are enclosed in an evacuated glass envelope so that the emitted electrons are able to move freely from one end of the tube to the other.

**Base:** Through this base, connections are made to various parts from cathode ray oscilloscope. Pins come out of this base and external connections are made.

#### **Advantages and disadvantages of CRT**

Monitors brightness can be increased easily

Colour features of a CRT are excellent

#### **Disadvantages:**

CRTs emit small amount of X-ray radiation which results in health hazard

CRTs operate at very high voltages resulting in overheating of the system or implosion

#### **Applications of CRTs**

In televisions

In computer monitors

As a display device in radars

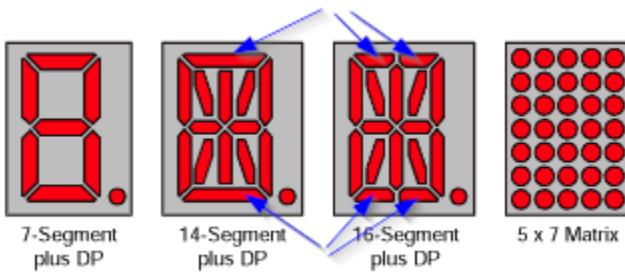
In cathode ray oscilloscopes

## Alphanumeric LCD Displays

Alphanumeric is the type of Latin and Arabic characters representing the numbers 0-9, the letters A-Z and some common symbols.

Most commonly used in cell phones, laptops, computers monitors, measurement equipment, electronic gadgets, home appliances, energy meters and other display systems.

The 14 segments can display any character of the alphabet and any number including decimal points.



CRTs draw more power than LCD and are also bigger and heavier. LCD's have made displays thinner than CRT's, the power consumption is lesser as it works on the basic principle of blocking light rather than dissipating.

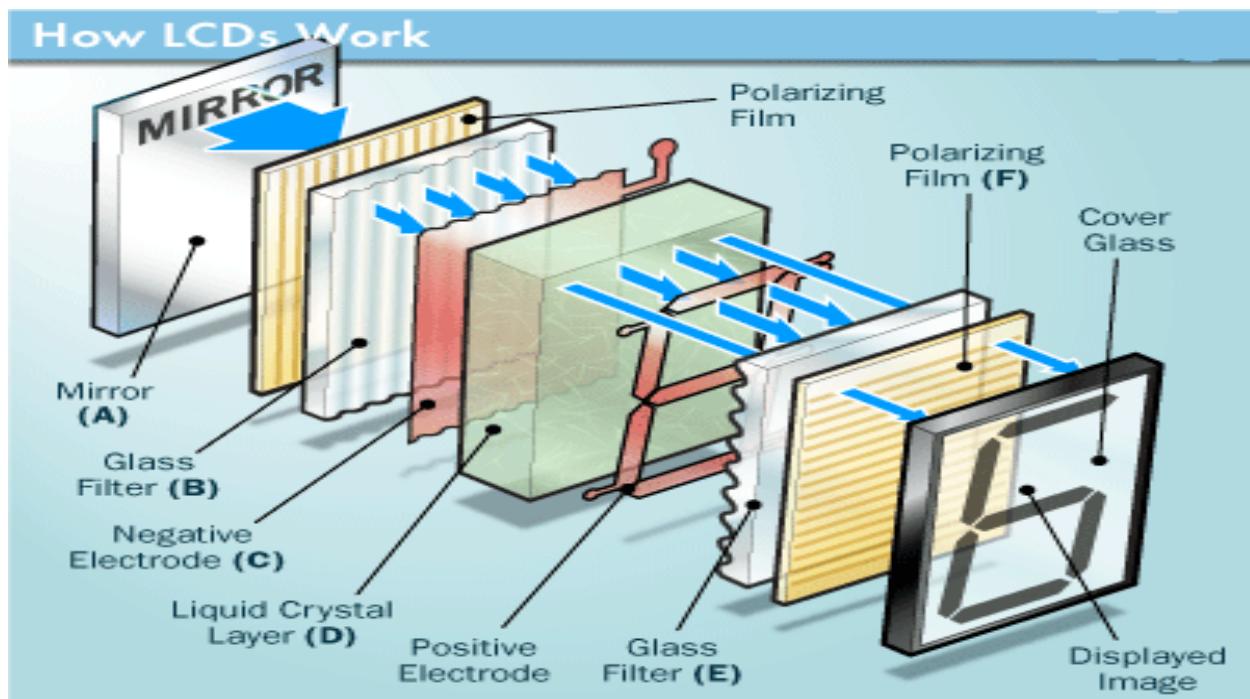
LCD is actually a combination of two states of matter – the solid and the liquid. They have both the properties of solids and liquids and maintain their respective states with respect to another. Solids usually maintain their state unlike liquids who change their orientation and move everywhere in the particular liquid.

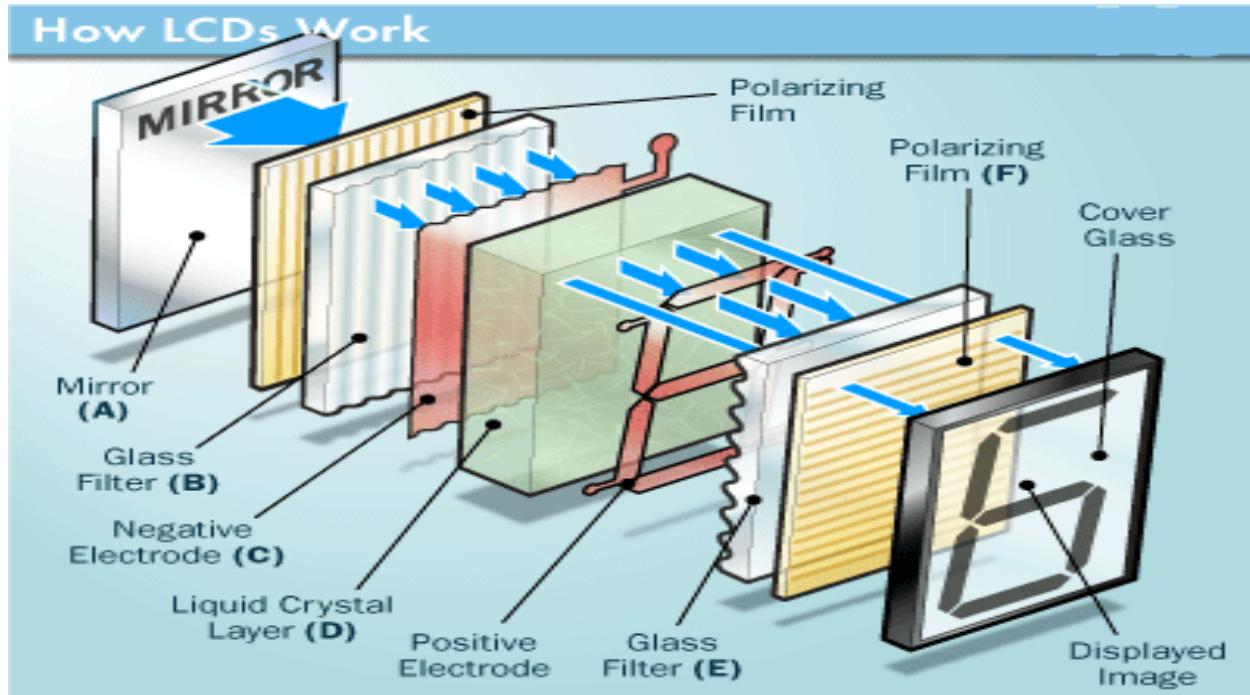
### Construction and working of LCD:

The main principle behind liquid crystal molecules is that when an electric current is applied to them, they tend to untwist. This causes a change in the light angle passing through them. This causes a change in the angle of the top polarizing filter with respect to it. So little light is allowed to pass through that particular area of LCD. Thus that area becomes darker comparing to others.

LCD consists of two polarized glass pieces. The glass which does not have a polarized film on it must be coated with a special polymer which creates microscopic grooves in the surface. It must also be noted that the grooves are on the same direction as the polarizing film. Then, add a coating of nematic liquid crystals to one of the filters. The grooves will cause the first layer of molecules to align with the filter's orientation. At right angle to the first piece, you must then add a second piece of glass along with the polarizing film. Till the uppermost layer is at a 90-degree angle to the bottom, each successive layer of TN molecules will keep on twisting. The first filter will naturally be polarized as the light strikes it at the beginning. Thus the light passes through each layer and is guided on to the next with the help of molecules. When this happens, the molecules tend to change the plane of vibration of the light to match their own angle. When the light reaches the far side of the liquid crystal substance, it vibrates at the same angle as the final layer of

molecules. The light is only allowed an entrance if the second polarized glass filter is same as the final layer. Take a look at the figure below.





### Alphanumeric LCD Displays

**CRT draws more power than LCD and are also bigger and heavier. LCD's have made displays thinner than CRT's. Even while comparing the LCD screen to an LED screen, the power consumption is lesser as it works on the basic principle of blocking light rather than dissipating. All of us have seen an LCD, but no one knows the exact working of it. Let us take a look at the working of an LCD.**

LCD is actually a combination of two states of matter – the solid and the liquid. They have both the properties of solids and liquids and maintain their respective states with respect to another. Solids usually maintain their state unlike liquids who change their orientation and move everywhere in the particular liquid.

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Thus the light passes through each layer and is guided on to the next with the help of molecules. When this happens, the molecules tend to change the plane of vibration of the light to match their own angle. When the light reaches the far side of the liquid crystal substance, it vibrates at the same angle as the final layer of molecules. The light is only allowed an entrance if the second polarized glass filter is same as the final layer. Take a look at the figure below.