

# XPS - X-ray photoelectron spectroscopy

## ① Principle:-

- It is based on Einstein's ~~photoelectric effect~~ <sup>photoelectric effect</sup>
- Due to bombardment of X-ray photon on sample surface, the inner shell ( $K$  and  $L$  shell electrons) are ejected out which are further analysed by the analyser.
- Kinetic Energy of the ejected electron is recorded by spectrometer.

Hence, the interaction takes place between the incident photon and the atoms in the surface (leading to emission of  $e^{-}(s)$ )

From the Kinetic Energy of the emitted electrons,  
The Binding Energy is calculated

② This relation is given by :-

$$E_k = h\nu - E_b - \phi$$

where  $E_k \rightarrow$  kinetic energy of ~~the~~ ejected electrons

$h\nu \rightarrow$  Energy associated with incident  $e^{-}$  (X-ray)

$E_b \rightarrow$  binding energy of ejected electron

$\phi \rightarrow$  work function of the instrument (Spectrometer)

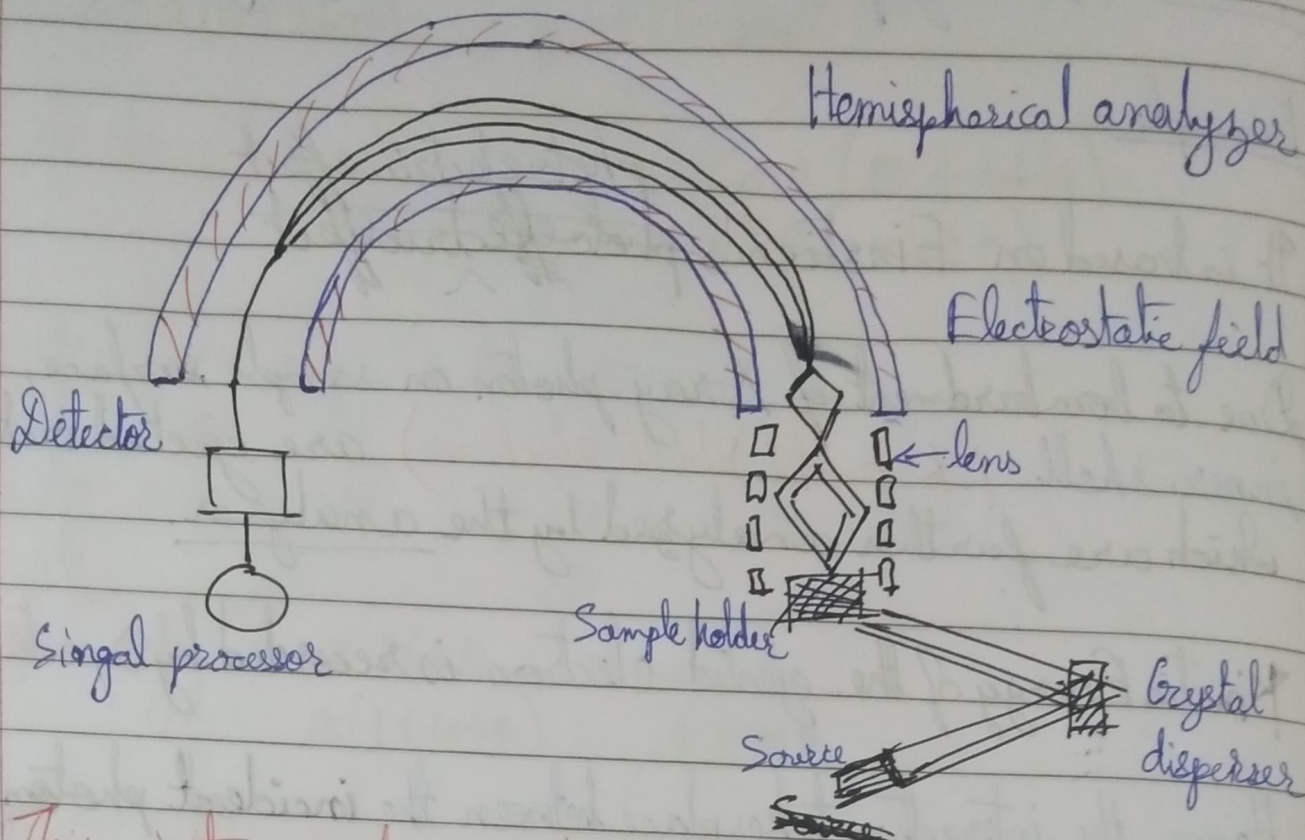
Binding Energy :-

Energy associated with attraction between electron & atomic nucleus

Binding Energy given by :-

$$E_b = h\nu - E_k - \phi$$

## ② Instrumentation:-



This instrument is made of the following components:-

- i) Source
- ii) Sample holder
- iii) Analyser
- iv) Detector
- v) Signal processor



i) Source:- The simplest X-ray photon source for XPS is X-ray tube equipped with ~~Mg~~ Mg or Al metal target.

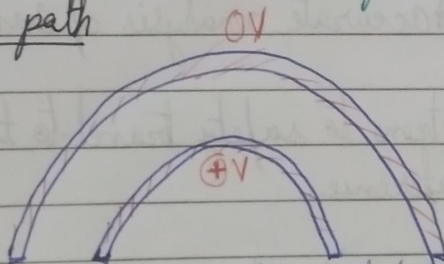
ii) Monochromator crystal can also be equipped with X-ray beam having bandwidth of  $0.3\text{ eV}$

iii) Sample holder:- It is located between the source and the entrance slit of the spectrometer.

Crystal disperser  $\rightarrow$  selects photons of known energy from the Source and only those photons are incident on the sample surface.

iii) Analyser:- It is located between ~~the~~ sample and the detector.

- It should be sensitive to identify the electron beam
- It is hemispherical in shape with very high electrostatic field applied on it.
- When electrons enter into the hemispherical analyser, it travels in a curved path



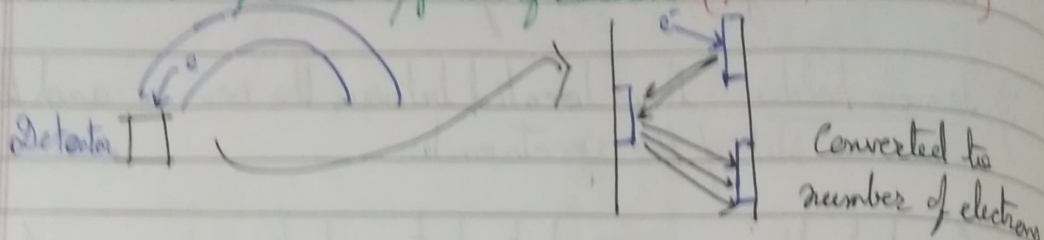
This analyser has 2 concentric metal cylinders  $\left\{ \begin{array}{l} \text{One at +ve voltage} \\ \text{Other at zero voltage} \end{array} \right.$

This creates an electric field bet<sup>n</sup> the two cylinders

- 1) If the electron velocity is too high, it will collide with outer cylinder
- 2) If the electron velocity is too low, it will collide with inner cylinder
- 3) If the electron travels at right velocity, only then it will go ~~thru~~ through the cylinder and reach the detector

iv) Detector - The electron multiplier is employed as detector due to its high sensitivity and convenience.

When electron pass through the electron multiplier, it gets converted into number of electrons/pulses of electrons ( $10^6 - 10^8$  electrons)



v) Signal Processor - Helps in analysing and interpreting signals that are detected during the experiment.

In this instrumentation, the experiment is conducted in a Ultra High Vacuum environment (UHV)

→ Advantages of this setup:-

1) Prevent Contamination of surface

2) Provide accurate analysis of sample

3) Allows electrons to safely travel to the detector without any interference.

(3) Working - When sample is kept in UHV is illuminated by photons of electrons energy ( $h\nu$ ), electrons from the sample is emitted in the form of photoelectron

When  $e^-$  leave the atom, some energy is consumed in overcoming the attraction from nucleus. This energy is called Binding Energy

XPS is obtained by determining the kinetic energy and number of electrons escaping from surface of sample



#### ④ Applications :-

i) ~~Helps~~ Helps us measure :-

- 1) Elemental composition
- 2) Empirical formula
- 3) Electronic state of metal

ii) ~~Identification~~ Identification of Active sites

iii) ~~All elements of~~ All elements of Periodic table can be determined except for Hydrogen and Helium

→ as they do not emit inner core electrons

iv) Determination of ~~surface~~ surface contamination in the sample