

## X-ray Photo Electron Spectroscopy (XPS) OR Electron Spectroscopy For Chemical Analysis (ESCA)

### Introduction :

A surface is a boundary layer between a solid and a vacuum, a gas or a liquid. Generally a surface is regarded as a part of a solid that differs in composition of the bulk of the solid.

Hence, the surface comprises not only the top layer of atoms but also of molecules of a solid, but also a transition layer having uniform composition that varies continuously from that of the outerlayer to that of the bulk. Thus, the surface may be many atomic layers deep. However, the difference in composition of the surface layer generally does not affect significantly, the overall composition of the bulk. This is due to the fact that the surface layer is generally a very small fraction of the total solid.

In recent years, a number of methods have been developed for surface characterisation.

The classical methods, already in use, provide much useful information about the physical nature of surfaces, but give much less information about their chemical nature.

Spectroscopic surface methods now provide useful information about the chemical nature of surfaces. These methods provide both qualitative and quantitative chemical information about the composition and surface layer of the solid.

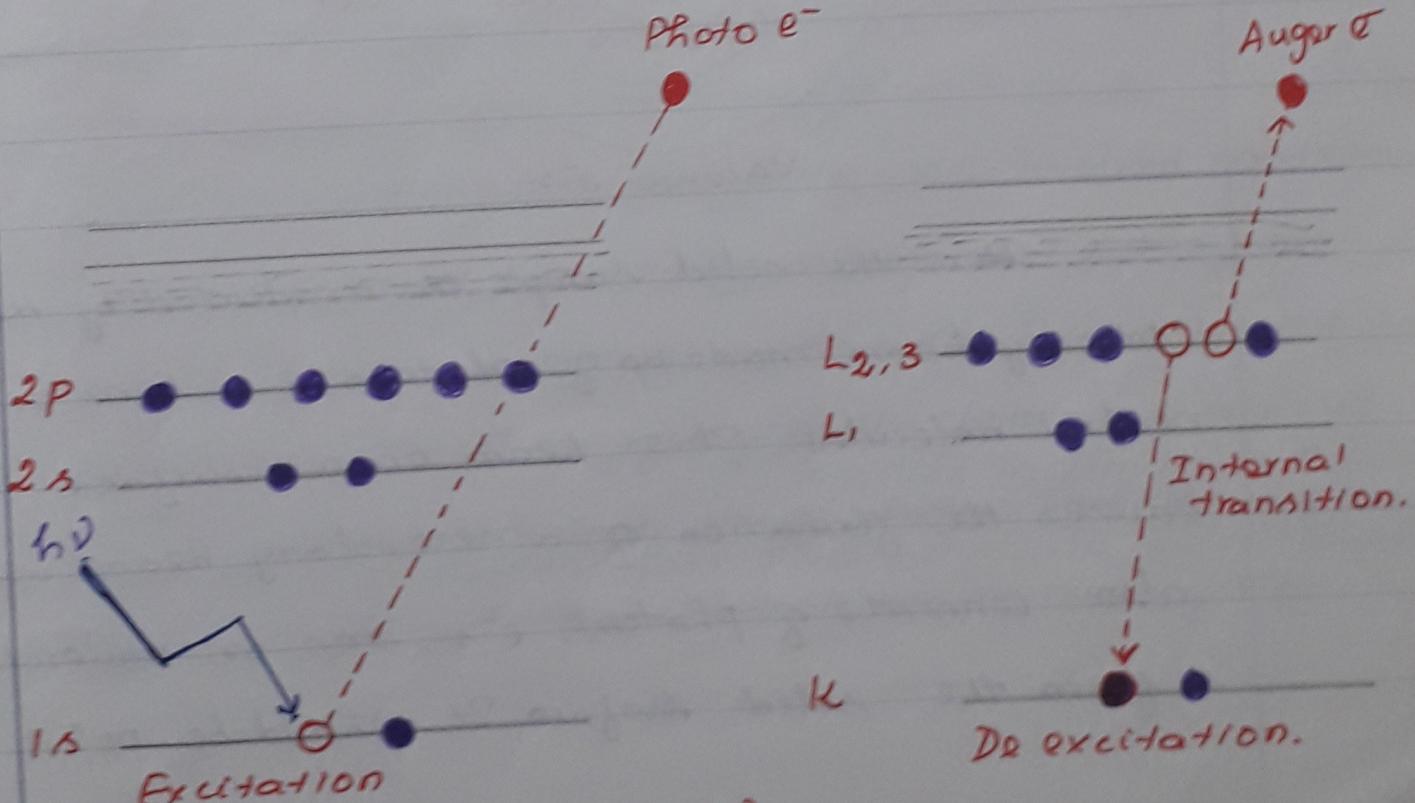
Various different phenomena can take place when a substance is bombarded by energetic particles or photons. The primary process is the ejection of  $e^-$ s from target atoms, which leaves vacancies. Following this process, either return to the normal configuration (relaxation) or emission process may occur.

- (i.e.) a) Characteristic x-rays may be emitted
- (or) b) Secondary  $e^-$ s (Auger  $e^-$ s) may be emitted or ejected.

Auger  $e^-$ :

When a core  $e^-$  is ejected whether by the action of an incident X-ray or by an energetic  $e^-$ , an  $e^-$  from a higher level will drop in to fill the vacancy. The energy released by this transition is sufficient to remove another  $e^-$  from the same shell in the atom.

Thus, if a  $1e^-$  is ejected by in the primary process, one  $2e^-$  may take its place in the K shell and at the same time a second  $2e^-$  is ejected from the atom. This is known as Auger effect.



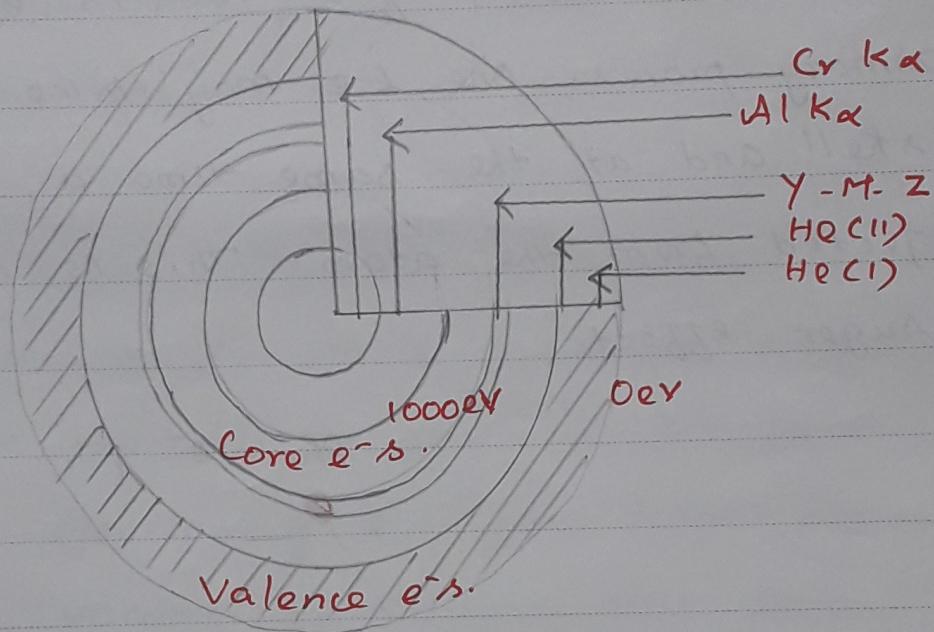
Sources :

(He(I) & He(II) - Singly & doubly ionised helium

for removing valency e<sup>-</sup>s to produce ions.

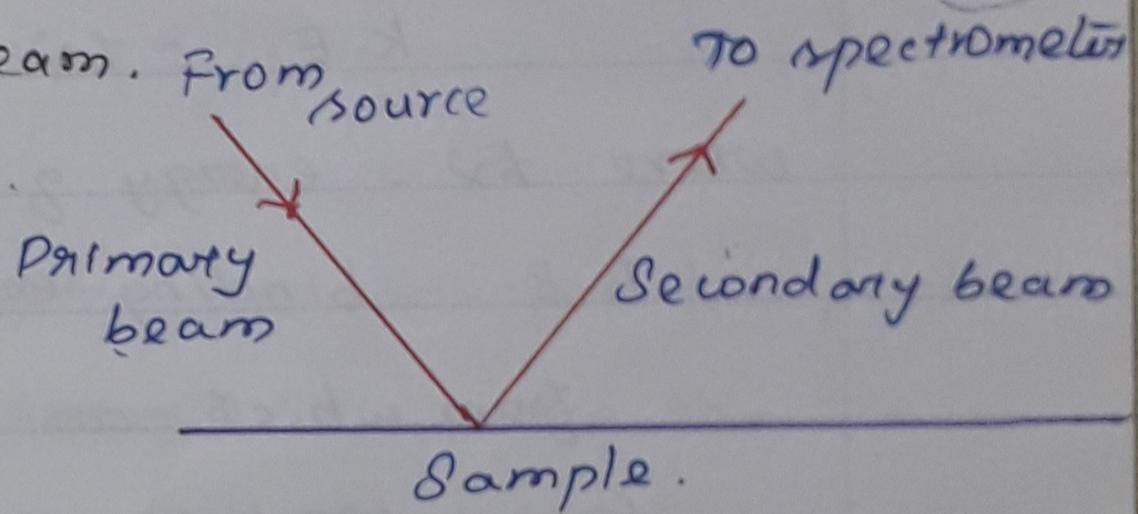
Yttrium- M- Zeta - X-rays can cause ejection of  
Outer core e<sup>-</sup>s.

Alk<sub>a</sub> or Cr K<sub>a</sub> - Most energetic radiations to  
reach the inner shells causing ionisation.)



Here the solid sample is irradiated by the primary beam made up of photons, e<sup>-</sup>s, ions or neutral molecules. This beam on a surface causes the formation of a secondary beam which also consists of photons, e<sup>-</sup>s, ions or molecules from the solid surface. It should be noted

that the type of particle making up the primary beam is not necessarily the same as the particle of the secondary beam.



| Method                                | Primary beam                         | Secondary beam    |
|---------------------------------------|--------------------------------------|-------------------|
| XPS (or) ESCA                         | X-ray Photons                        | e <sup>-</sup> s. |
| Auger Electron Spectroscopy (AES)     | e <sup>-</sup> s (or) X-ray Photons. | e <sup>-</sup> s  |
| Ultraviolet Photo electron Spec (UPS) | UV photons                           | e <sup>-</sup> s. |

## XPS Principle.

It is a surface sensitive quantitative spectrometric technique that measures the elemental composition, empirical formula, chemical & electronic state of the elements.

It is obtained by irradiating the material with a beam of X-rays and simultaneously measuring the kinetic energy and the number of  $e^-$ s that escapes from the top 0 - 10 nm of the material being analysed. The penetration depth of these photons in solids is limited to few microns. Thus interactions takes place between the incident photons and the atoms in the surface leading to the photoelectric emission of  $e^-$ s. From the kinetic energy of the emitted  $e^-$ s, the binding energy is calculated as follows

$$E_{\text{Binding}} = E_{\text{Photon}} - (E_{\text{kinetic energy}} + \phi)$$

$E_{\text{Binding}}$  - Binding energy of  $e^-$

$E_{\text{Photon}}$  - Energy of incident photons.

$E_{\text{kinetic}}$  - Energy of emitted  $e^-$ s measured by the instrument.

$\phi$  - work function dependent on the spectrometer & the material.

## Instrumentation:-

XPS contains the following equipments.

1. Source
2. Sample holder
3. An energy analyser
4. An  $e^-$  detector.
5. A high vacuum system.

### Source :

The simplest X-ray sources for XPS spectrometers are X-ray tube equipped with Mg or Al targets and suitable filters. Al & Mg targeted tubes are generally used without a monochromator because of the high intensity and narrow bands &  $k\alpha$  lines of

these light elements. It should be noted that narrow bands are desirable because they give rise to enhanced resolution.

### Sample holder:

Solid samples are mounted in a fixed position as close to photon or  $e^-$  source and the entrance slit of the spectrometer as possible.

### Energy Analyser: (Monochromator) ~~or~~ ~~etc~~

(The energy analyser <sup>is placed</sup> between the sample and detector) has a more strict efficiency requirement than the filters, because the  $e^-$  beam magnitude will be less intense. Hence, (it should be very sensitive to identify the  $e^-$  beam that is coming out of the sample).

Most widely used monochromators utilise either cylindrical or spherical electrostatic fields. (Most of the electron spectrometers are of hemispherical type in which the  $e^-$  beam is deflected by an electrostatic magnetic field in such a manner that the electrons travel in a curved path.)

Energy analyser

~~EHA~~ has two concentric metal cylinders at different voltages. One of the metal cylinders will have a positive voltage and the other will have 0 voltage. This will create an electrical field between the two cylinders.

When the  $e^-$  pass through the metal cylinder they will collide with one of the cylinders or they will just pass through.

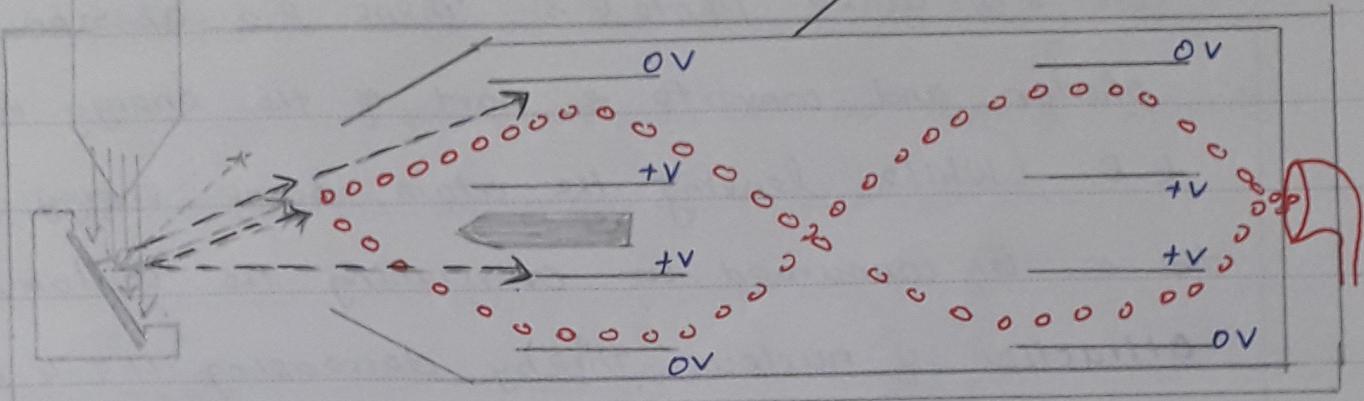
1) If the  $e^-$ 's velocity is too high, it will collide with the outer cylinder.

2) If it is going too slow then it will collide with the inner cylinder.

3) Only the  $e^-$  with the right velocity will go through the cylinder to reach the detector.)

With the change in cylinder voltage, the acceptable K.E will change and then we can count how many  $e^-$ 's have that K.E to reach the detector.

## Electron Pathway through CMA.



### Detectors:

The electron multiplier is usually employed as a detector, because of its sensitivity and convenience.

### High vacuum system: (UHV) Ultra High Vacuum.

The ultra high vacuum environment will prevent the contamination of the surface and aid an accurate analysis of the sample.

It will allow the photo e<sup>-</sup>s to travel from the surface of the sample to the detector without striking a gas atom.

### Working:

In XPS, when the sample kept in ultra high vacuum is illuminated by the photons of energy ( $\lambda\gamma$ ), the surface of the sample emits

core  $e^-$ s called Photo  $e^-$ s) These  $e^-$ s absorbs a photon and converts the part of the energy into K.E. While leaving the atom, some energy of the  $e^-$  is consumed in overcoming the coulombic attraction of nucleus thereby decreasing its K.E. At this time the outer orbitals readjust, reducing the energy to and delivering the extra energy to the outgoing  $e^-$ s. Then, the XPS spectrum is obtained by determining the K.E. of the no. of  $e^-$ s escaping from upper 0 to 10 nm of sample under investigation.

### Applications:

#### 1. Qualitative determination:

↳ Chemical state, surface adsorption, surface state, chemical structure, chemical bonding etc.

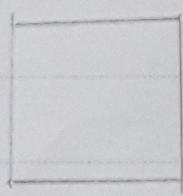
#### 2. Quantitative determination:

~~of various~~ Determination of elemental composition of various inorganic and organic materials.

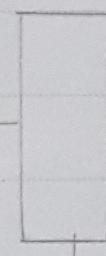
#### 3. Useful in the identification of elements in the periodic table.

## XPS Instrument.

### Computer system.

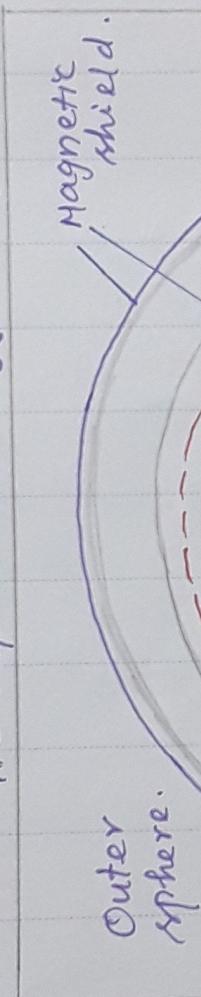


### Analyser control 1.



multichannel  
plate electron  
multiplier.

### Hemispherical energy analyser.



### Inner sphere.

Lenses for energy  
adjustment.

Lenses for analysis  
area definition.

Position sensitive  
detector.

Sample.

X-ray  
source.