

# X-ray Photoelectron Spectroscopy (XPS)

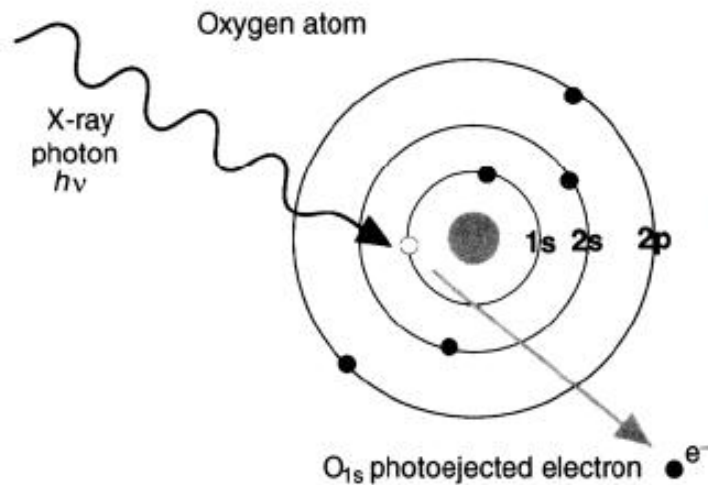
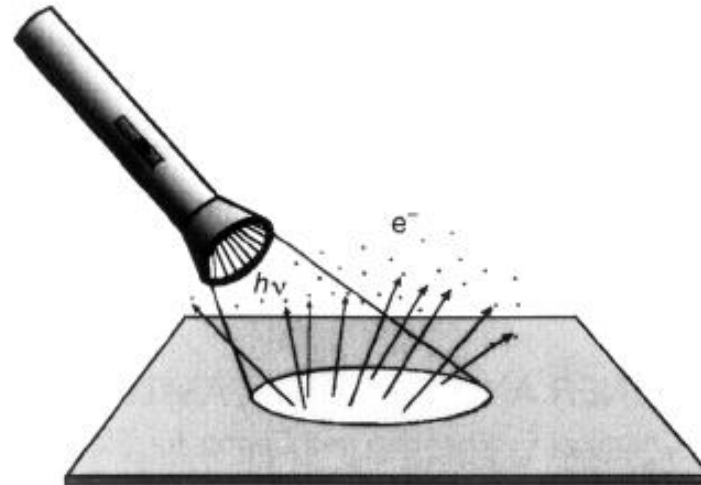
Principle  
Working  
Applications  
Instrumentation

## Introduction

### Photoelectric effect

Photoelectric effect

Einstein, Nobel Prize 1921

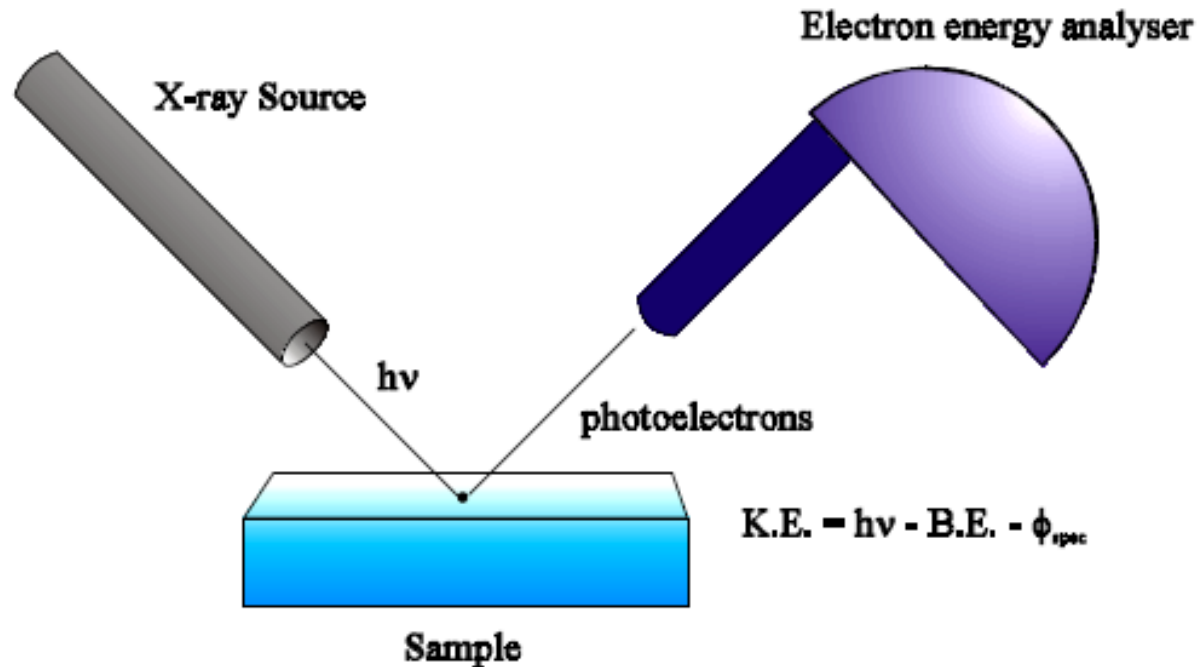


Photoemission as an analytical tool

Kai Siegbahn, Nobel Prize 1981

XPS, also known as ESCA, is the most widely used surface analysis technique because of its relative simplicity in use and data interpretation.

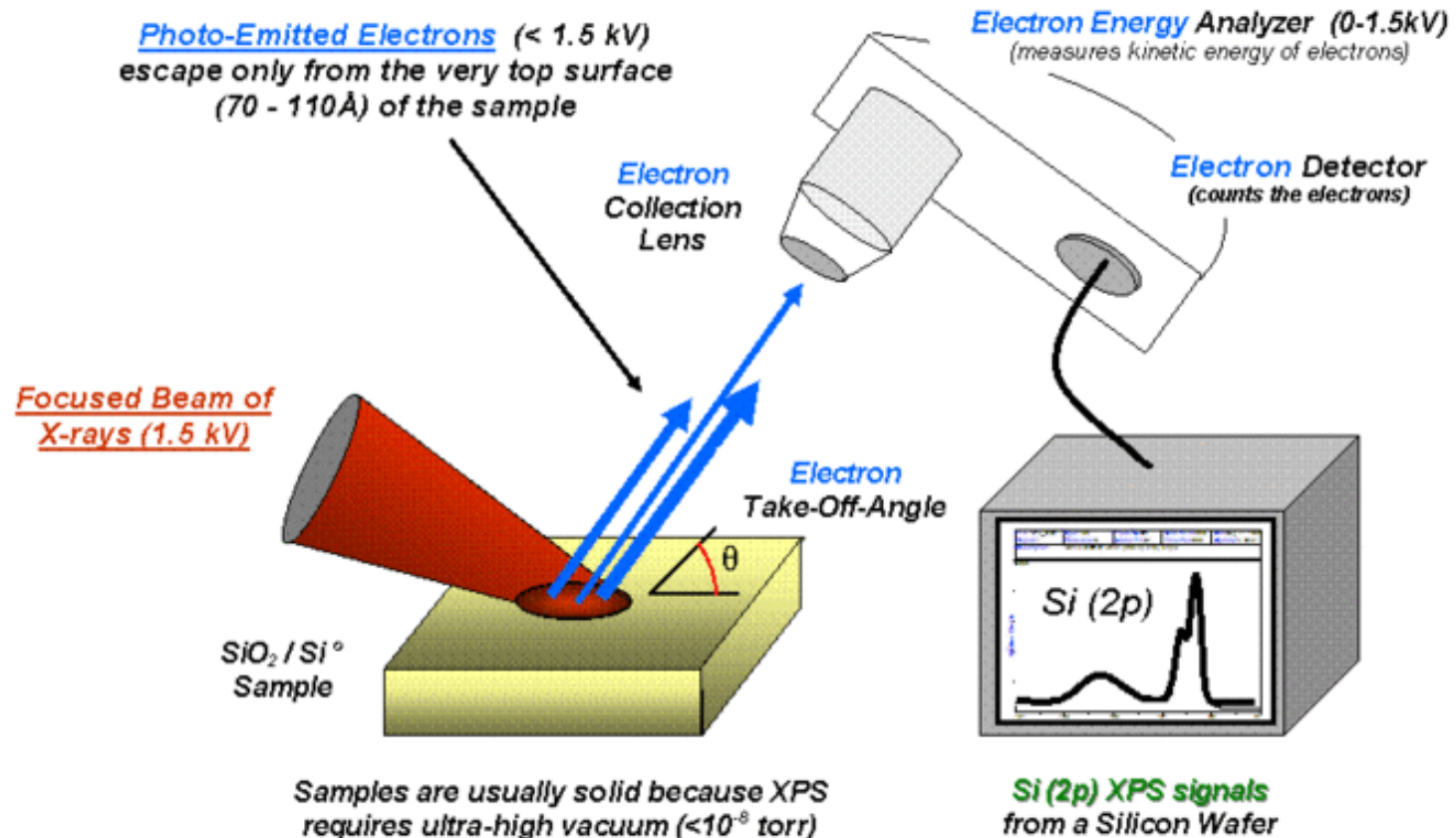
- XPS** X-ray Photoelectron Spectroscopy
- ESCA** Electron Spectroscopy for Chemical Analysis
- UPS** Ultraviolet Photoelectron Spectroscopy
- PES** Photoemission Spectroscopy



# Theory of xps

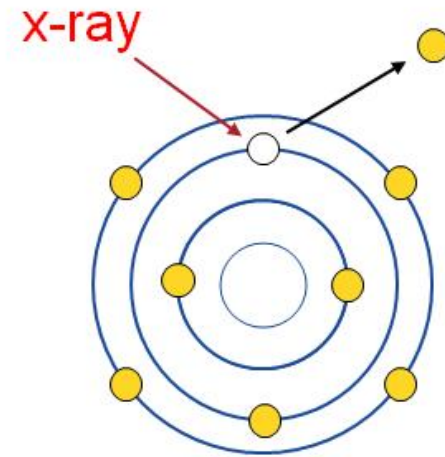
- Based on the photoelectric effect
- Emitted x-rays from the machine are focused towards the sample
- The x-rays have sufficient energy ( $h\nu$ ) to ionize core electrons (BE) and give them excess kinetic energy (KE):

- $KE$  is the response with  $h\nu$  provided from the machine. BE can be determined
- Identification of elements possible as binding energies for the core electrons are unique for every element



# *X-Ray Photoelectron Spectroscopy (XPS)*

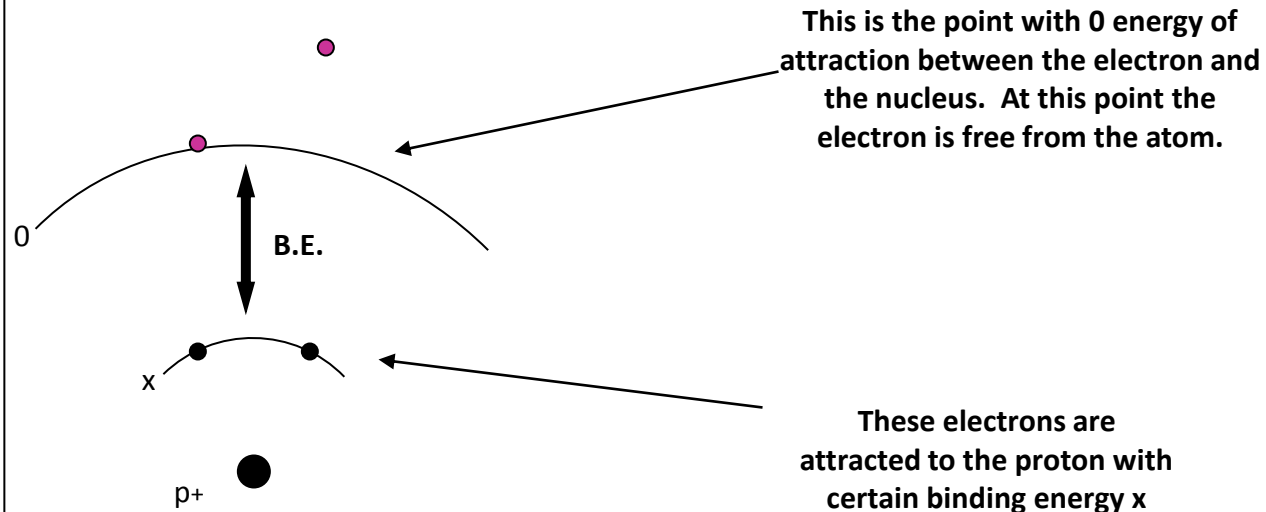
- An x-ray beam usually comprised of k-alpha x-rays is focused on the sample.
- The absorption of incident x-rays results in the ejection of electrons.
- The energy of the ejected electrons is measured by the detector.



# Binding Energy (BE)

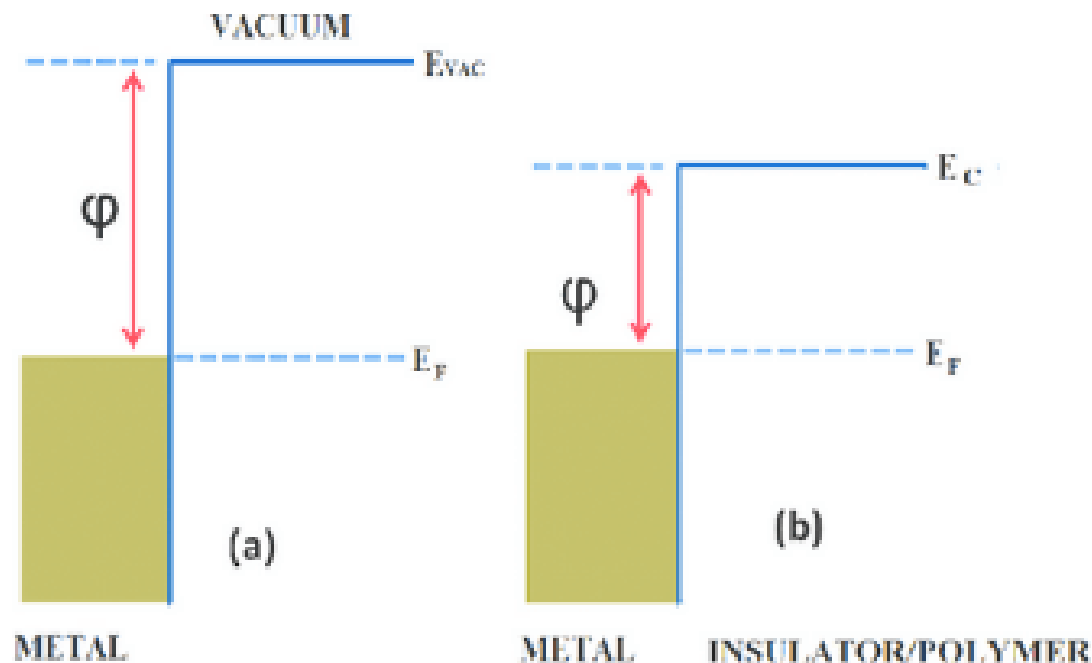
The Binding Energy (BE) is characteristic of the core electrons for each element. The BE is determined by the attraction of the electrons to the nucleus. If an electron with energy  $x$  is pulled away from the nucleus, the attraction between the electron and the nucleus decreases and the BE decreases. Eventually, there will be a point when the electron will be free of the nucleus.

**Definition:** Electron binding energy, also called [ionization potential](#), is the energy required to remove an electron from an [atom](#), a molecule, or an [ion](#). In general, the binding energy of a single proton or neutron in a nucleus is approximately a million times greater than the binding energy of a single electron in an atom.



## Work Function Definition

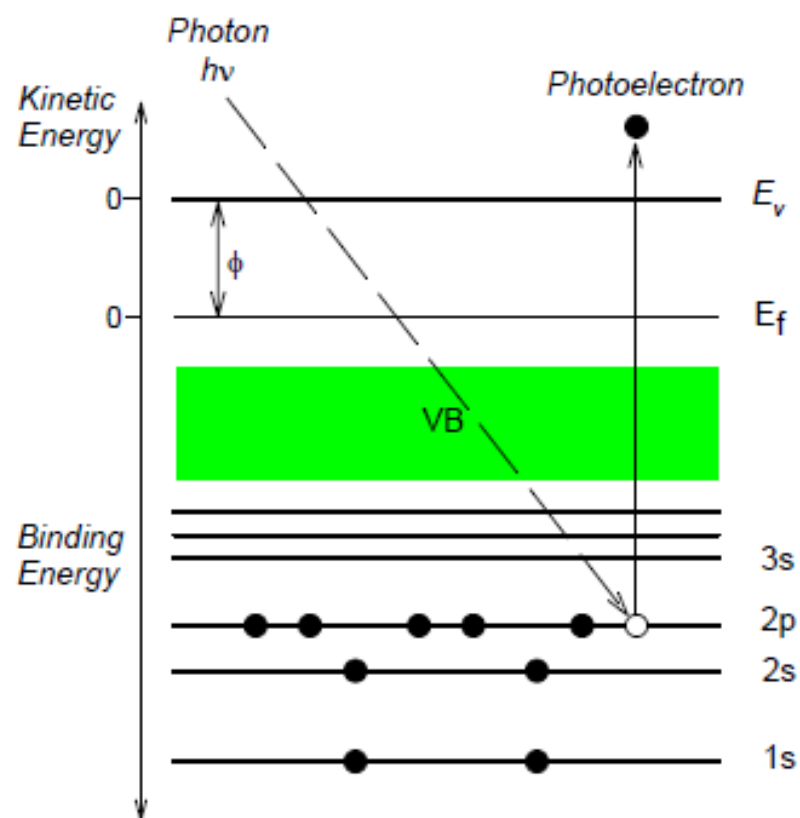
The **work function** (or **workfunction**) is defined as the minimum amount of thermodynamic work (i.e. energy) required to remove an electron from a solid to a point in the vacuum immediately outside the solid surface. The symbol for work function is  $\Phi$  (uppercase Phi of the Greek alphabet).



The minimum energy required just to escape an electron from a metal surface is known as work function.

# Analytical Methods

## --- X-ray Photoelectron Spectroscopy (XPS)



$$KE = h\nu - (E_B + \phi)$$

**XPS spectrum:**  
Intensities of photoelectrons  
versus  $E_B$  or  $KE$

- Elemental identification and chemical state of element
- Relative composition of the constituents in the surface region
- Valence band structure

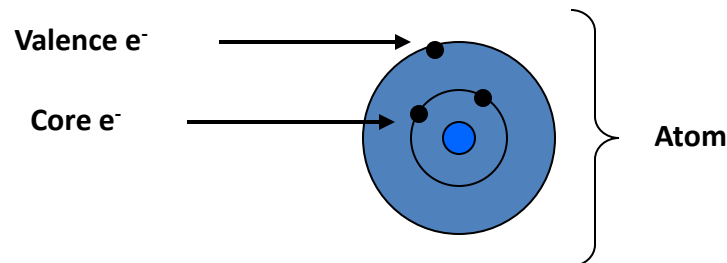


# X-Rays

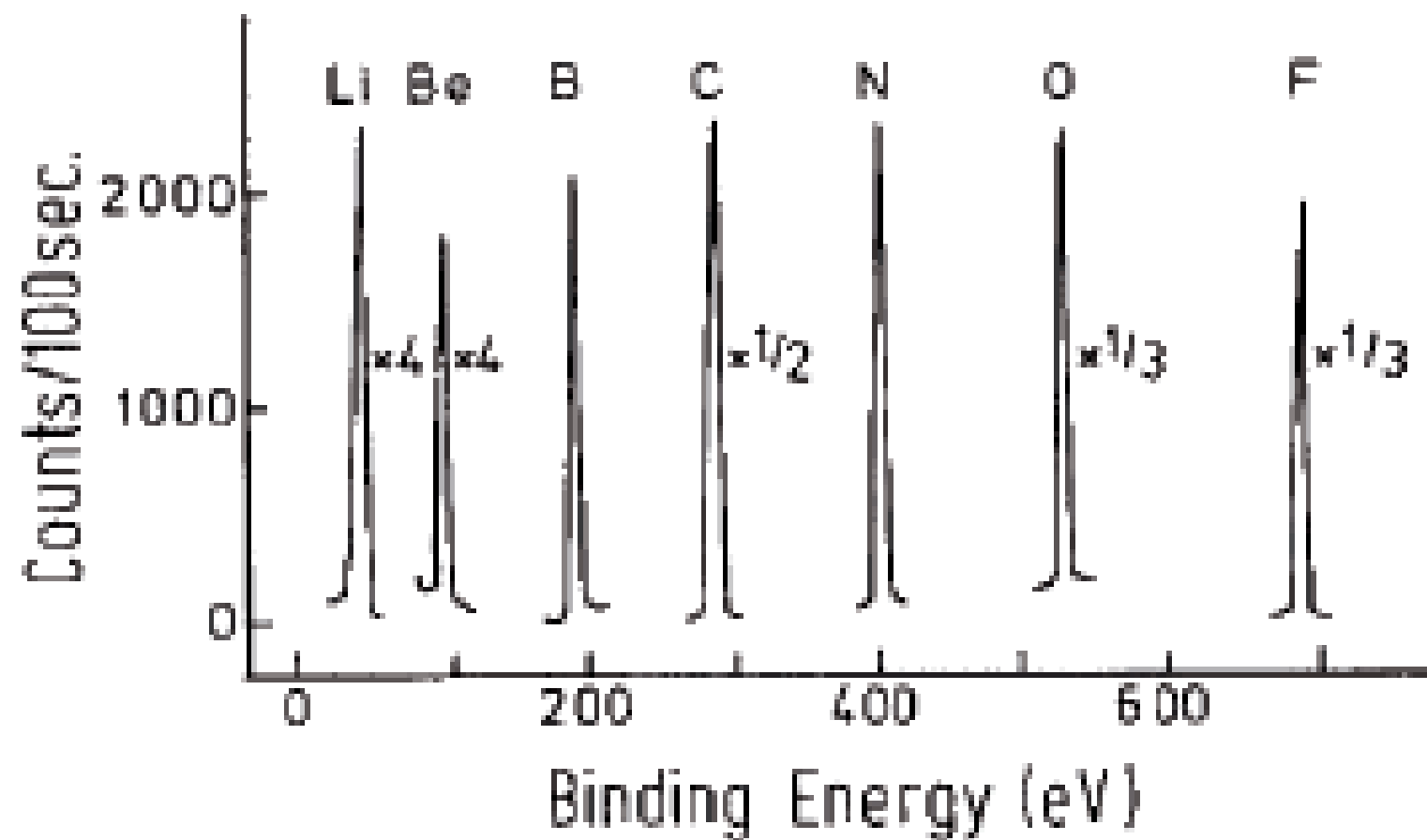
- Irradiate the sample surface, **hitting the core electrons ( $e^-$ )** of the atoms.
- The **X-Rays penetrate** the sample to a depth on the order of a micrometer.
- Useful  $e^-$  signal is obtained only from a depth of around **10 to 100 Å** on the surface.
- The X-Ray source produces photons with certain energies:
  - **MgK $\alpha$**  photon with an energy of **1253.6 eV**
  - **AlK $\alpha$**  photon with an energy of **1486.6 eV**
- Normally, the sample will be radiated with photons of a single energy (MgK $\alpha$  or AlK $\alpha$ ). This is known as a **monoenergetic X-Ray beam**.

# Why the Core Electrons?

- An electron near the Fermi level is far from the nucleus, moving in different directions all over the place, and will not carry information about any single atom.
  - Fermi level is the highest energy level occupied by an electron in a neutral solid at absolute 0 temperature.
  - Electron binding energy (BE) is calculated with respect to the Fermi level.
- The **core e<sup>-</sup>s are local close to the nucleus and have binding energies characteristic of their particular element.**
- The core e<sup>-</sup>s have a higher probability of matching the energies of AlK $\alpha$  and MgK $\alpha$ .



# 1s BINDING ENERGIES

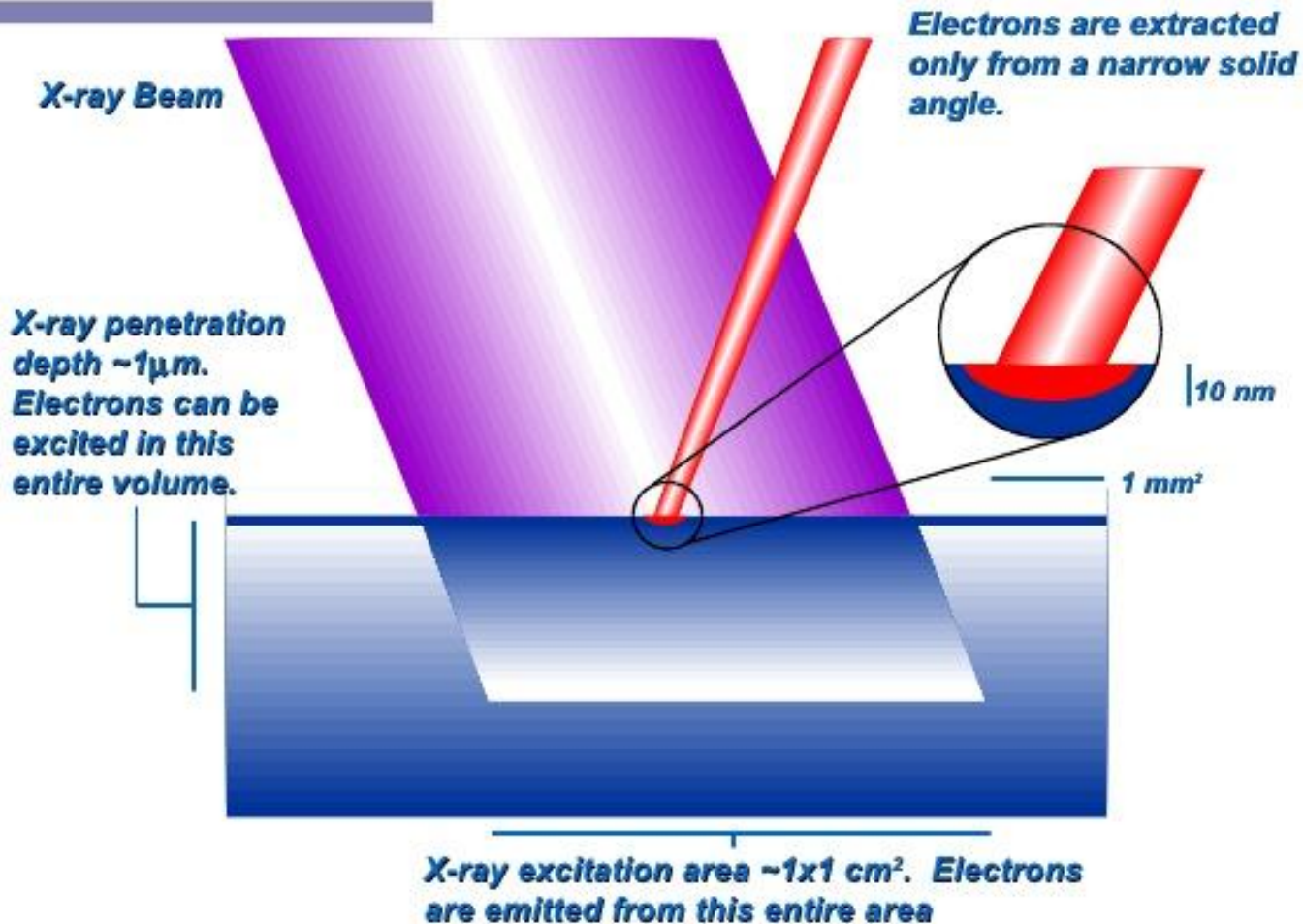


# How Does XPS Technology Work?

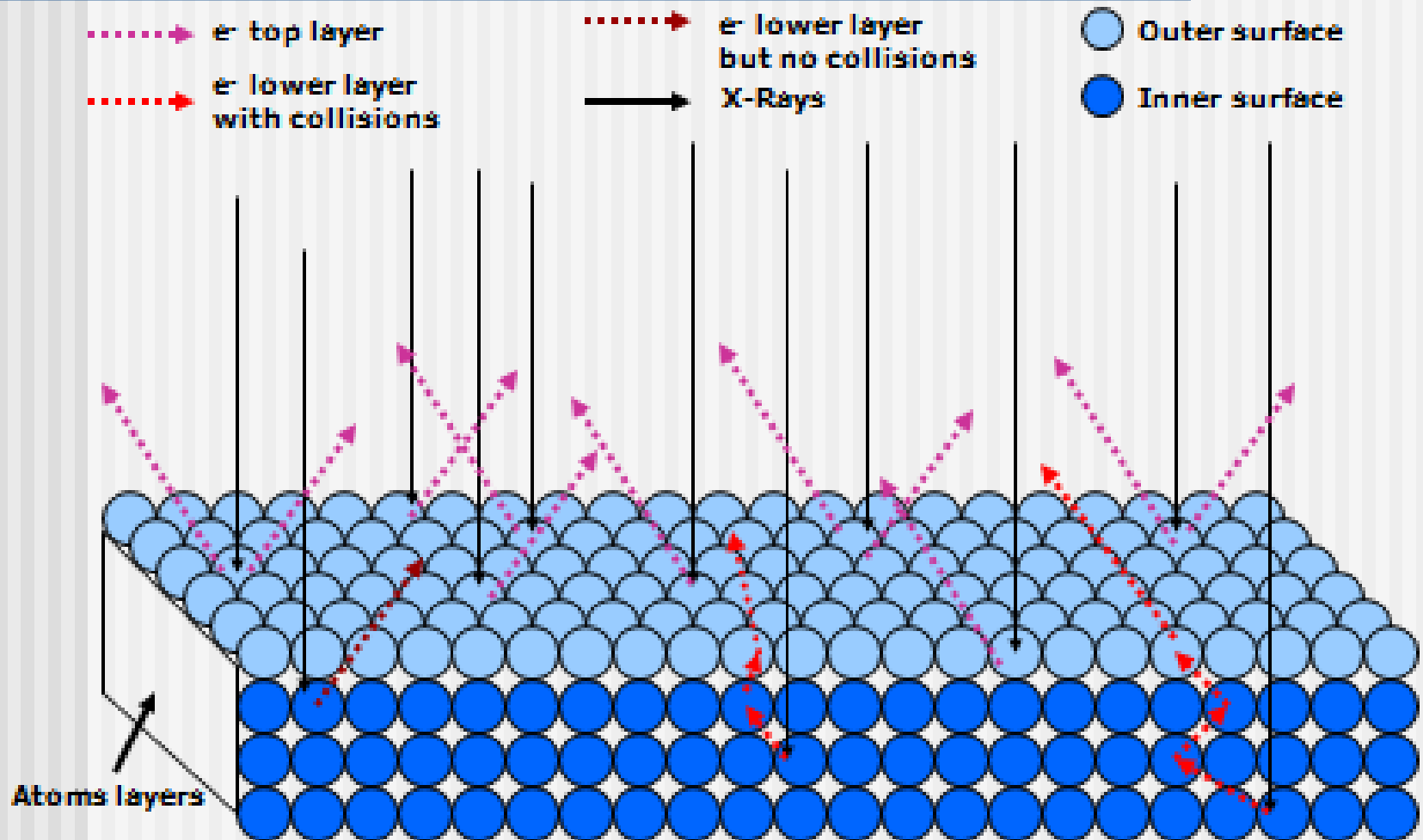
- A **monoenergetic x-ray** beam emits photoelectrons from the surface of the sample.
- The X-Rays either of two energies: **Al  $K_{\alpha}$**  (1486.6eV) **Mg  $K_{\alpha}$**  (1253.6 eV)
- The x-ray photons **penetrate** about a micrometer of the sample
- The XPS spectrum contains information only about the **top 10 - 100 Å** of the sample.
- **Ultrahigh vacuum** environment to eliminate excessive surface contamination.
- Concentric Hemispherical Analyzer (**CHA**) measures the **KE** of emitted e<sup>-</sup>s.
- The **spectrum plotted** by the computer from the analyzer signal.
- The **binding energies** can be determined from the peak positions and the **elements** present in the sample **identified**.

# X-ray Photoelectron Spectroscopy

## Small Area Detection



# X-Rays on the Surface



# XPS Technology

- Consider as non-destructive
  - because it produces soft x-rays to induce photoelectron emission from the sample surface
- Provide information about surface layers or thin film structures
- Applications in the industry:
  - Polymer surface
  - Catalyst
  - Corrosion
  - Adhesion
  - Semiconductors
  - Dielectric materials
  - Electronics packaging
  - Magnetic media
  - Thin film coatings

## It is used to measure:

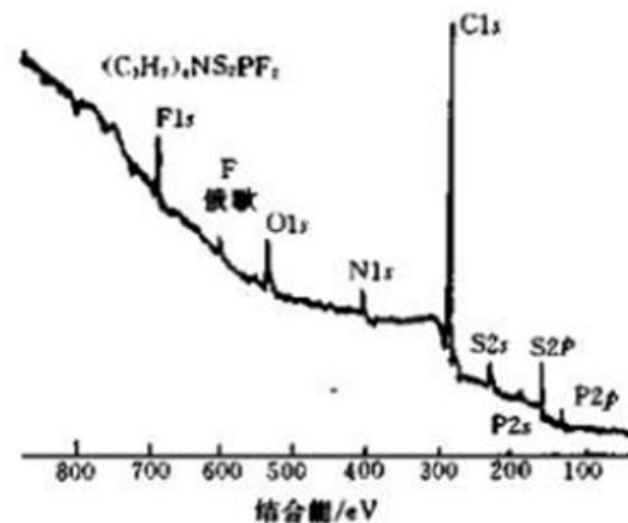
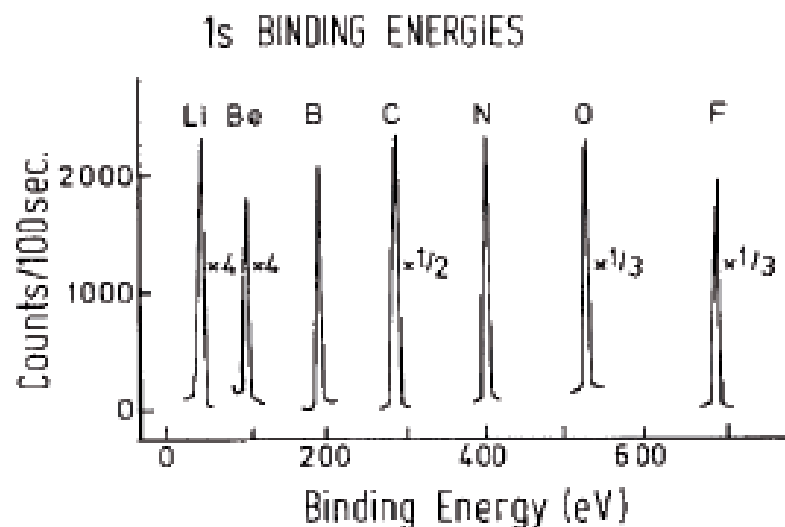
- **elemental composition** of the surface (top 1–10 nm usually)
- empirical formula of pure materials
- elements that **contaminate** a surface
- **chemical or electronic state** of each element in the surface
- The **binding energy of one or more electronic states**
- uniformity of elemental composition across the top surface (or **line profiling** or **mapping**)
- uniformity of elemental composition as a function of ion beam etching (or **depth profiling**)



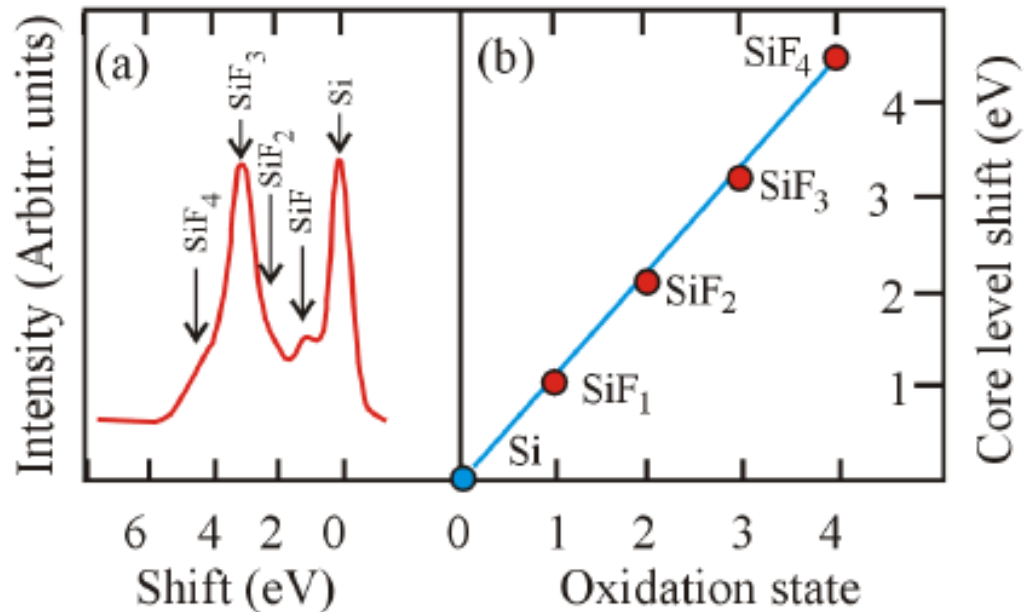
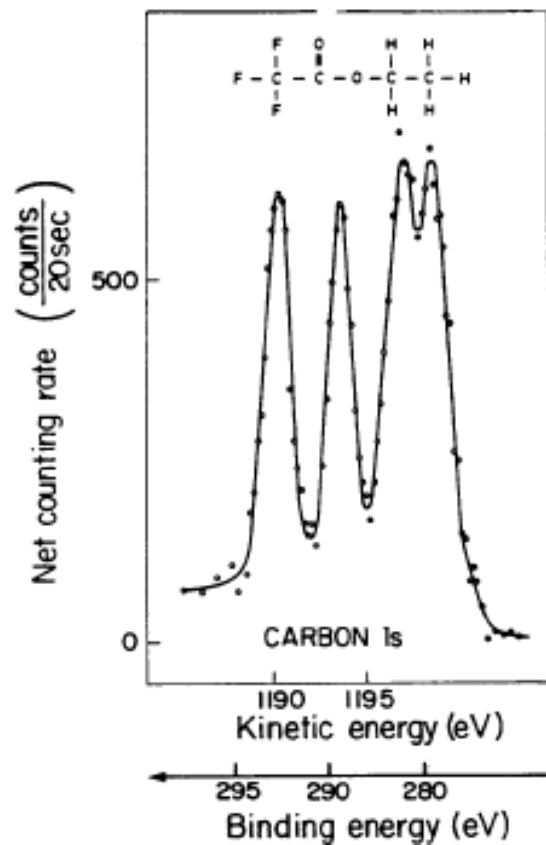
**1. Qualitative analysis:** The binding energies of electrons are characteristic of specific elements. So, the peaks (i.e. the binding energies) in the photoelectron spectrum dictate the elements present in the sample.

e.g.

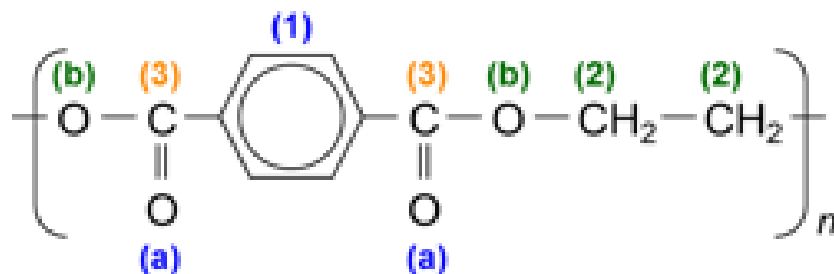
Element	Li	Be	B	C	N	O	F
1s (B.E. in eV)	50	110	190	280	400	530	690



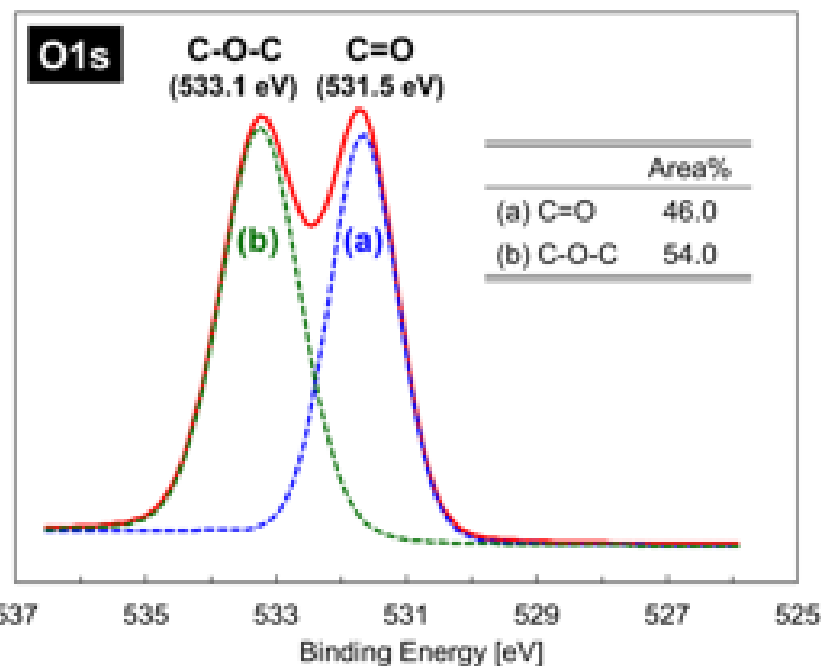
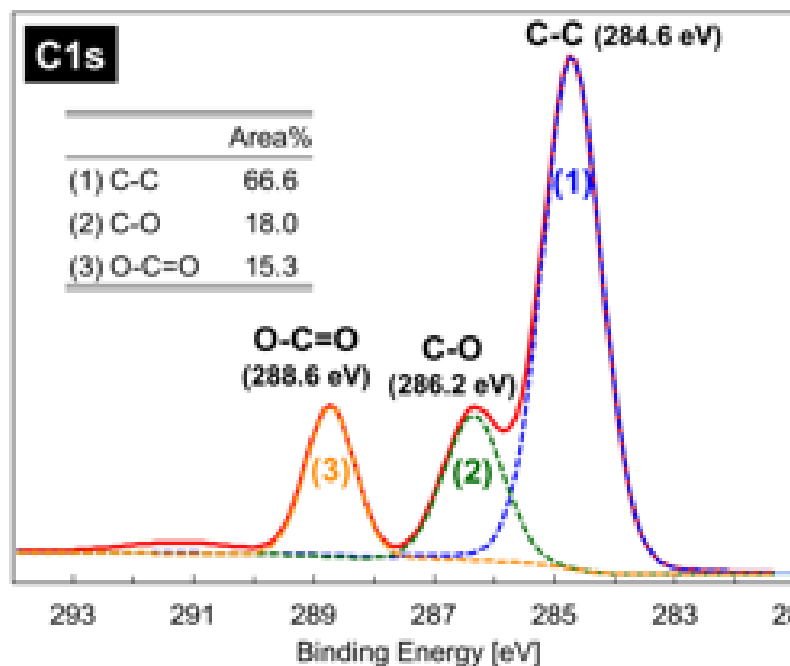
# Examples of Chemical Shifts



**2. Quantitative Analysis:** Converting the peak intensities or peak area to atomic concentrations give the elemental composition of the sample. For example,

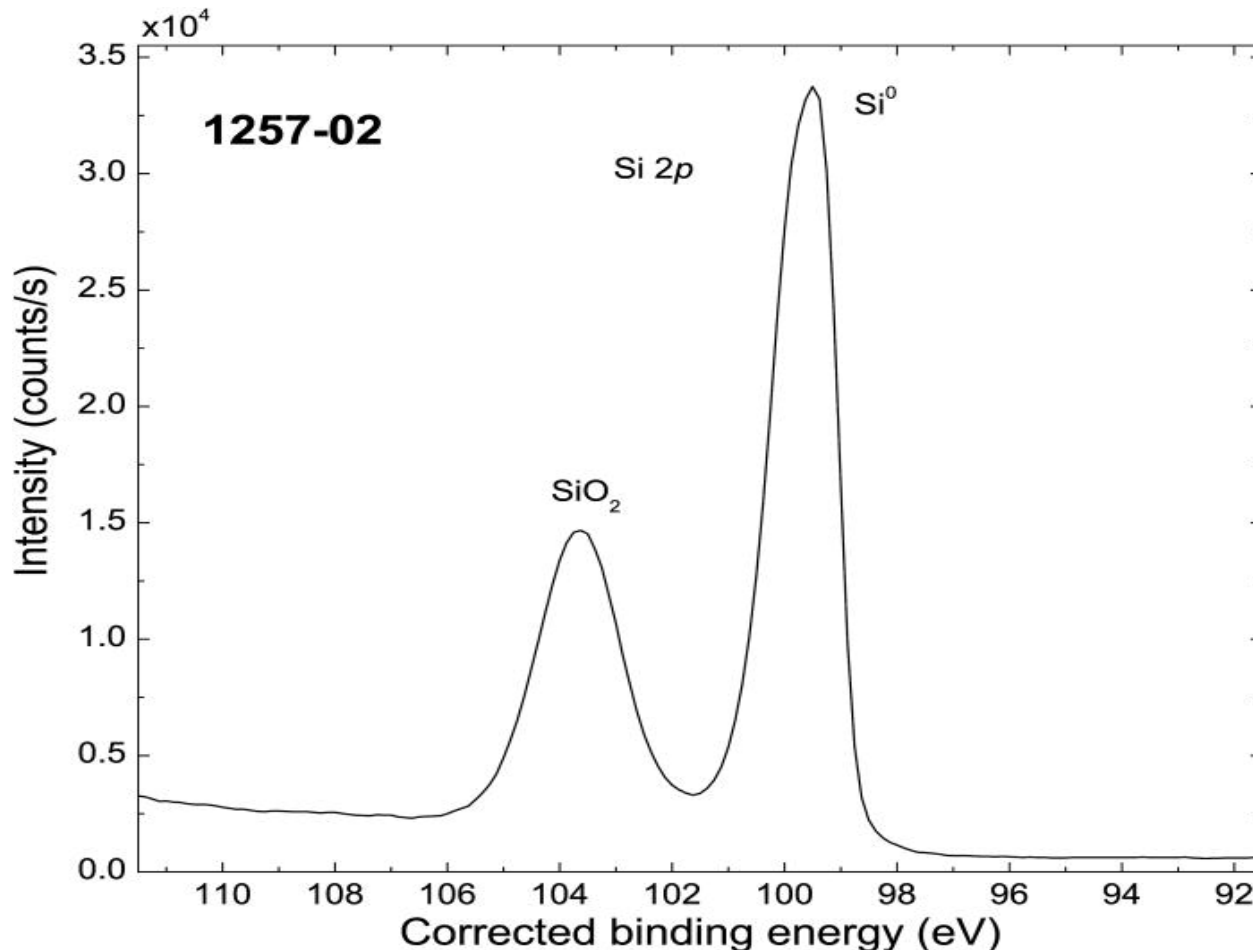


Structure of PET

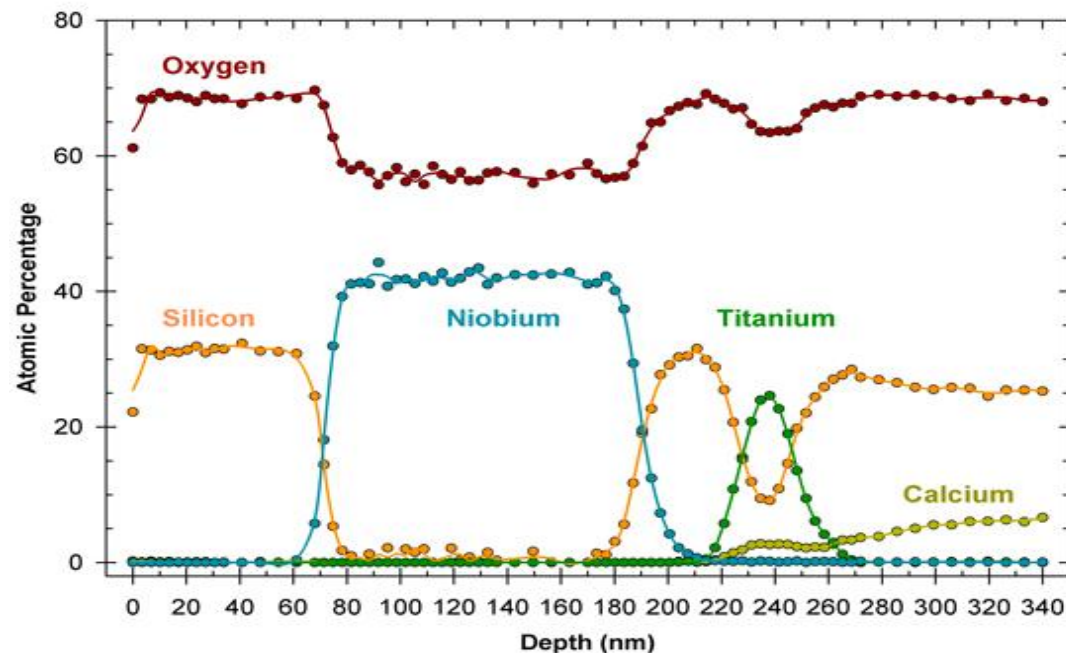
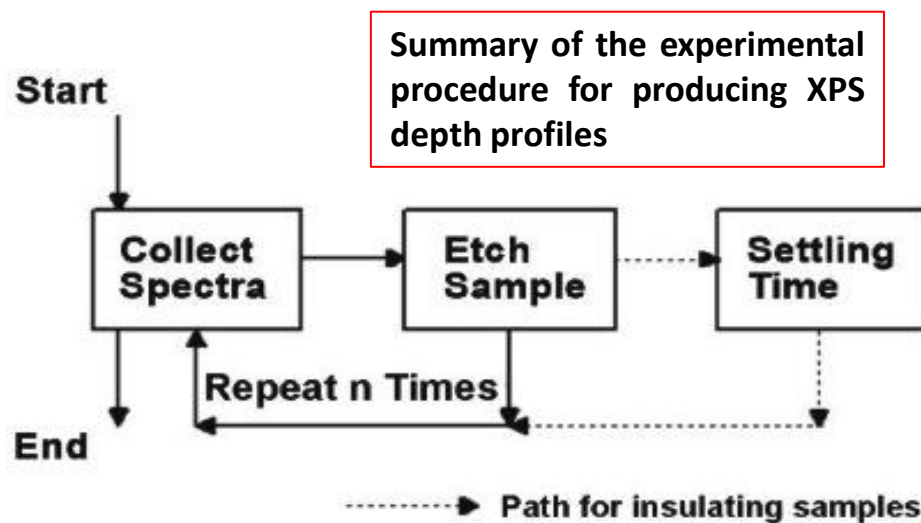
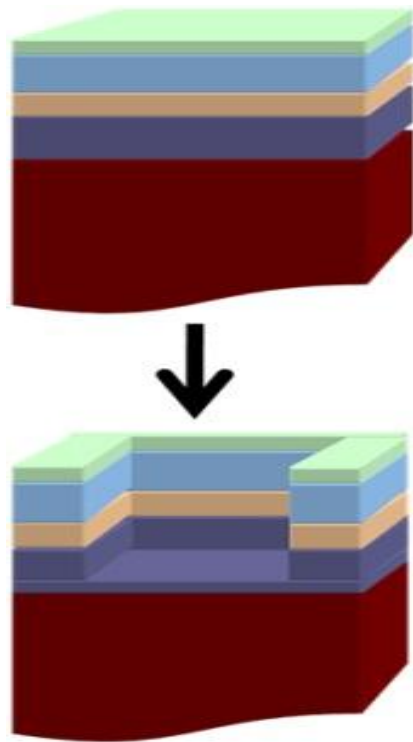


XPS spectra of PET

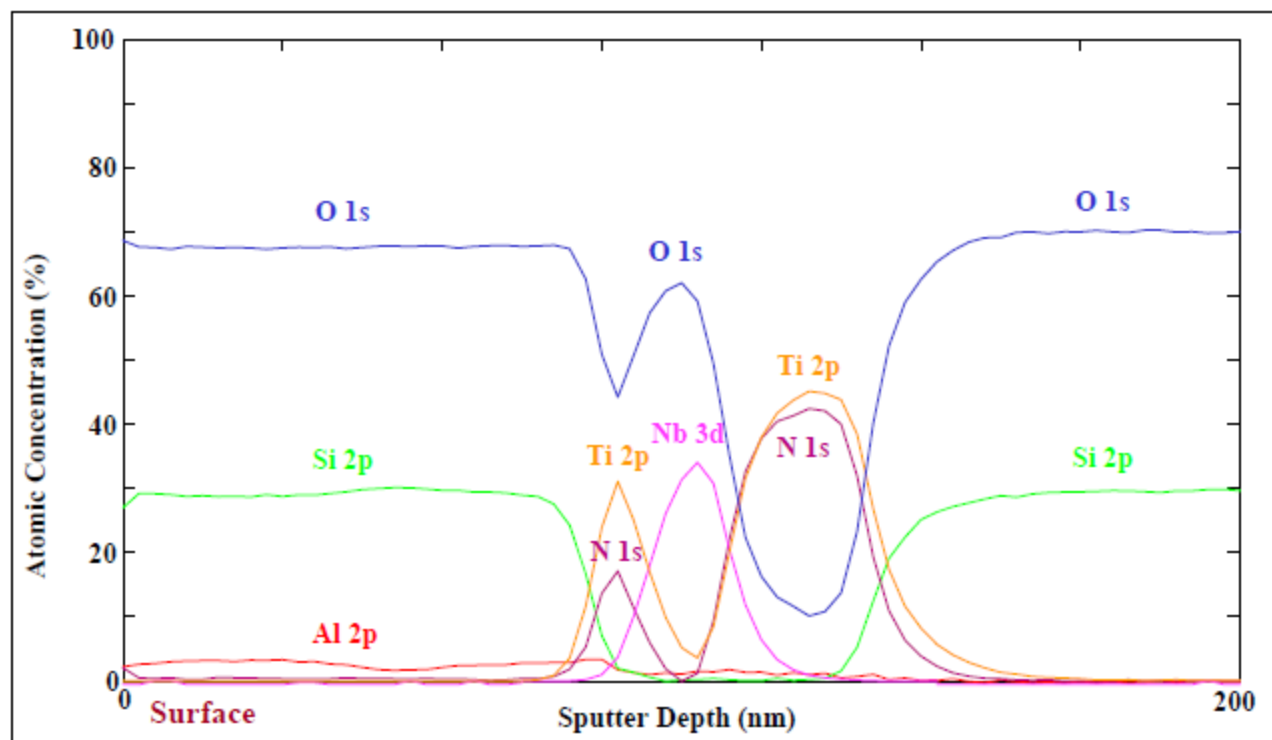
**3. Determination of oxidation state:** Higher the oxidation state, higher is the B.E. e.g shifts in peak positions indicate the formation of oxides on Silicon. As shown below,  $\text{SiO}_2$  i.e. Si (+IV) peak appears at higher B.E. (~104 eV) compared to  $\text{Si}(0)$  (~100 eV). From the value of the shift in peak position, the oxidation state of the element can be determined.



**4. Depth profiling:** Determination of uniformity of composition as a function of depth of sample using ion beam etching.



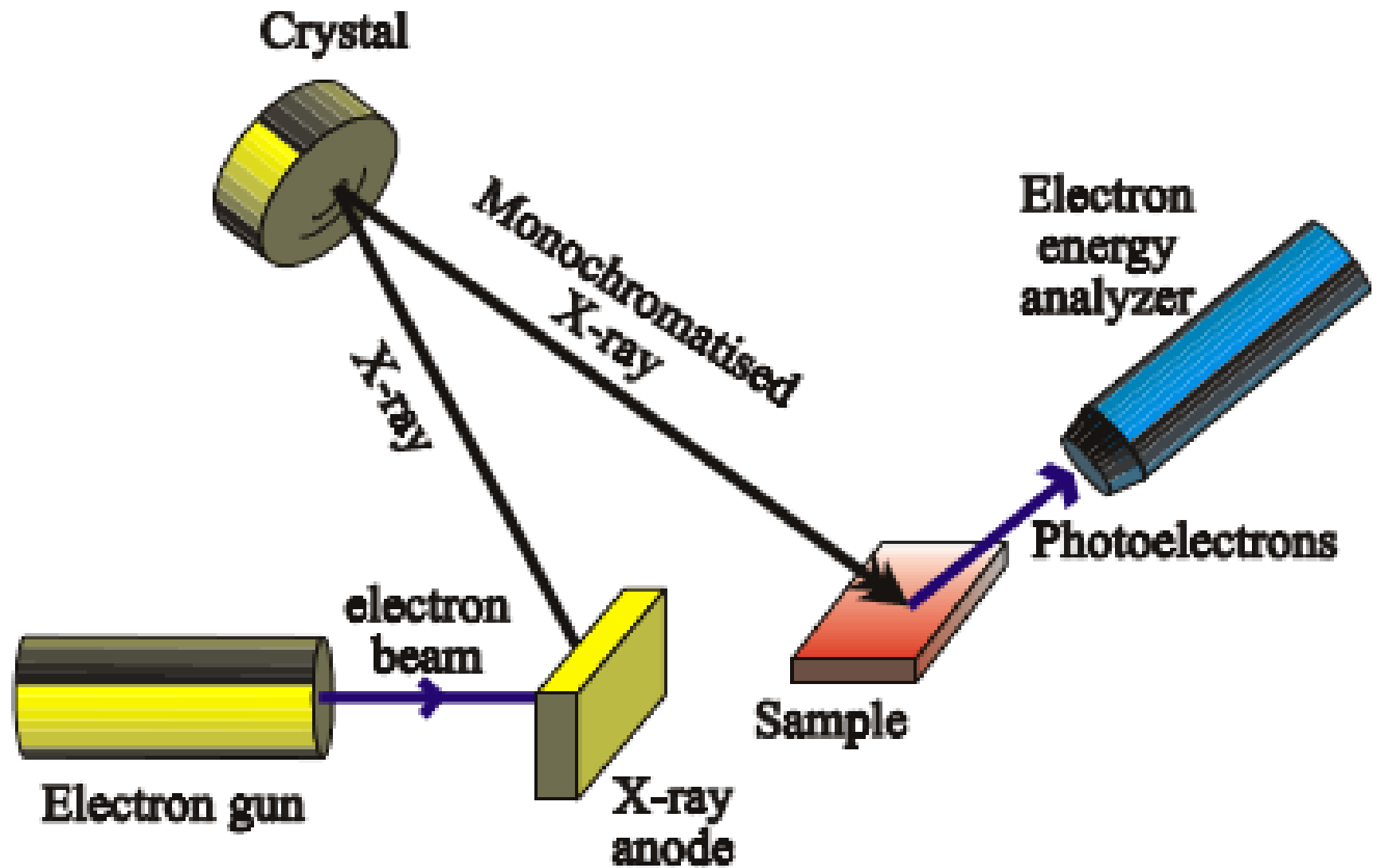
## Depth profile of Architectural Glass Coating



**5. Line Profiling:** Determination of uniformity of the composition across the surface.

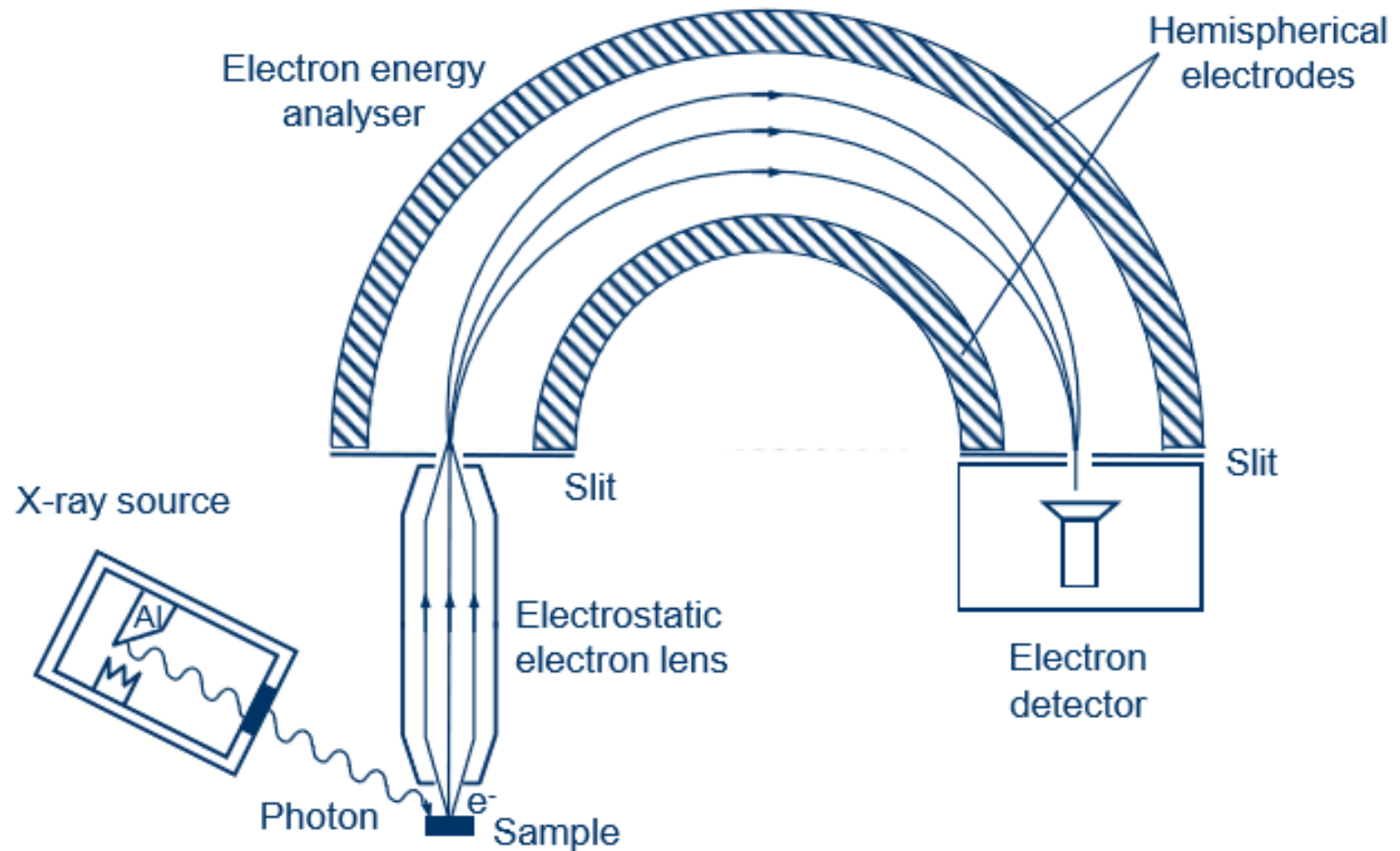
6. **Determination of contamination** of the surface.

# XPS-Instrumentation





# XPS-Instrumentation



Number of emitted electrons measured  
as function of their kinetic energy

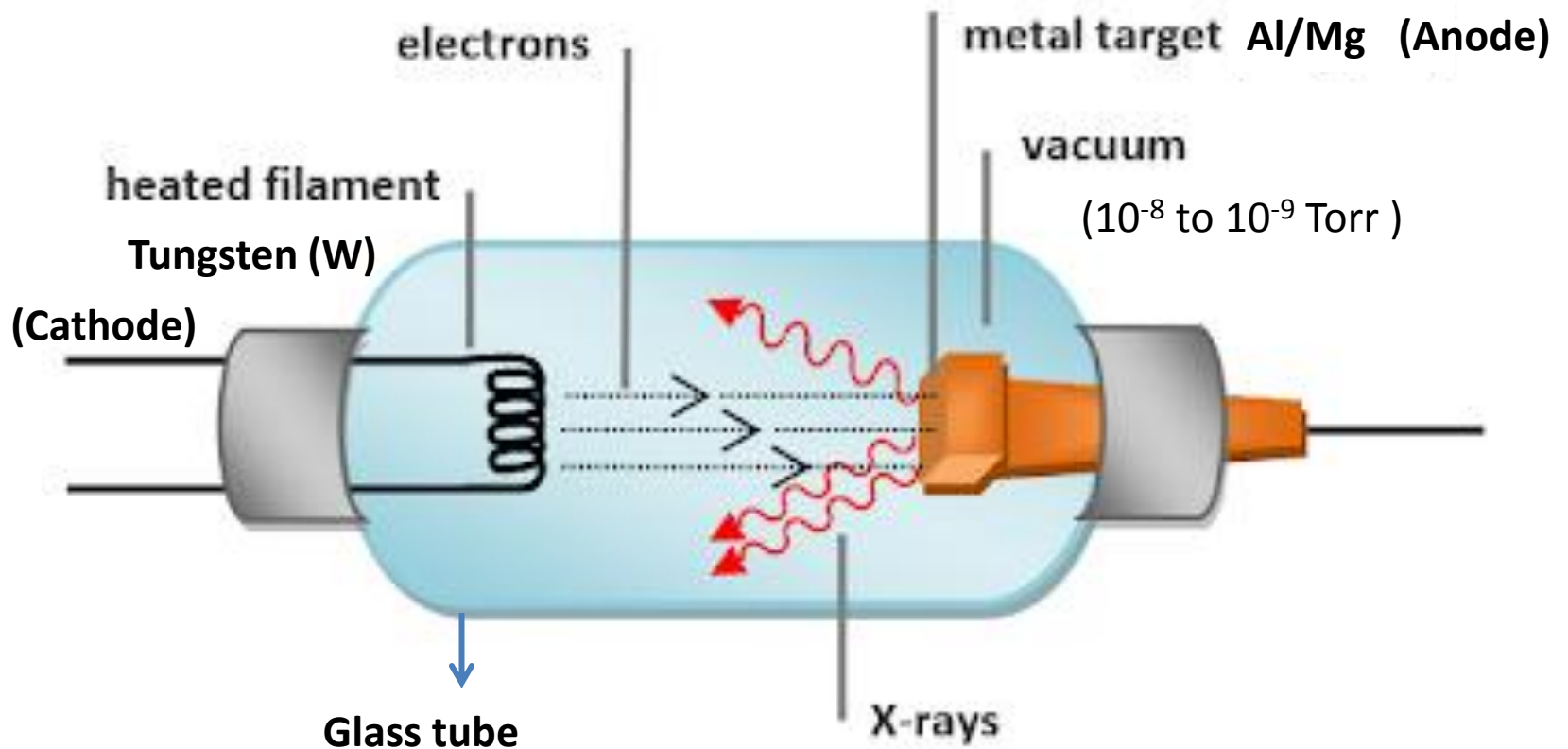
## ➤ **Four components of photoelectron spectrometer**

- **X-ray source**
- **X-ray Monochromator**
- **Electron energy analyzer and**
- **Electron detector**

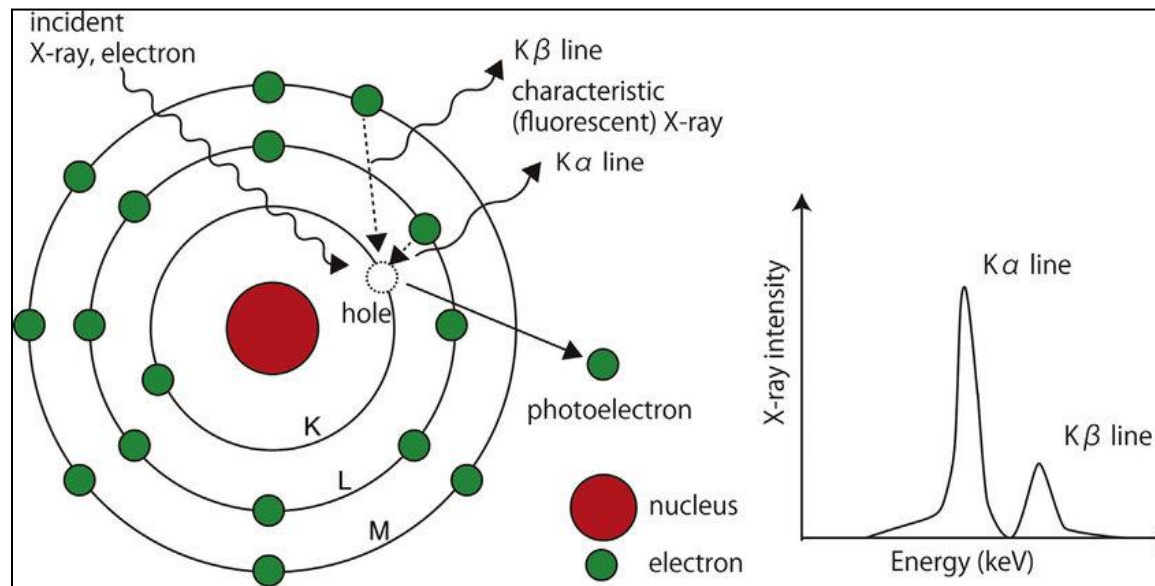
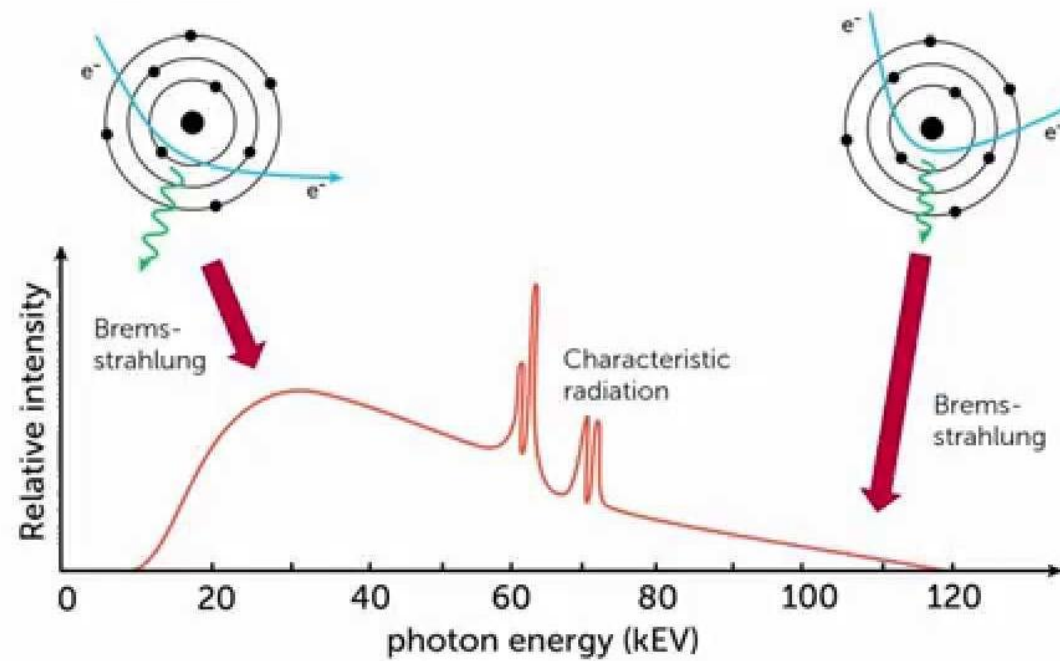
## The twin anode X-ray source:

- The choice of **anode material** for XPS **determines the energy** of the X-ray generated.
- It must be of **high enough photon energy** to excite an intense photoelectron peak from all elements of the periodic table.
- The **most popular** anode materials are aluminium and magnesium.
- X-rays are generated by bombarding an anode material with **high-energy electrons**. The electrons are emitted from a thermal source, usually in the form of an **electrically heated tungsten filament**.
- A typical X-ray source consists of a **twin anode of Al or Mg** giving Al  $K_{\alpha}$  (0.834 nm) or Mg  $K_{\alpha}$  (0.989 nm) photons of energy 1486.6 eV and 1253.6 eV respectively.

# Generation of X-rays

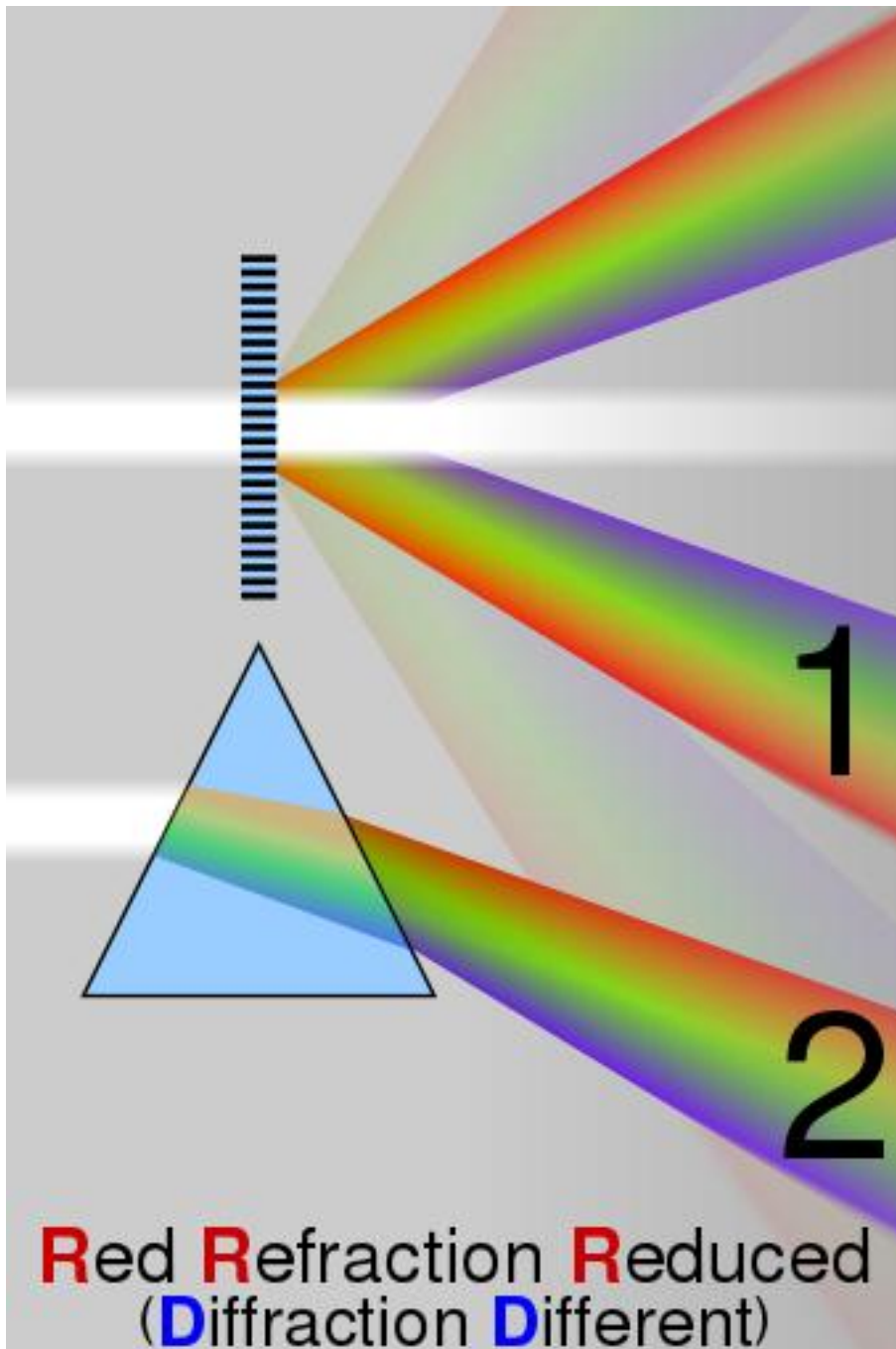


# X-ray generation - spectrum



## X-ray Monochromator:

- The purpose of an X-ray monochromator is to produce a **narrow X-ray line** by using **diffraction in a crystal lattice**.
- All commercially available X-ray monochromators used for XPS employ a **quartz crystal** as the **diffraction lattice**.
- The reasons for choosing an X-ray monochromator are:
  1. Reduction in X-ray line width results in narrower XPS peaks and consequently gives better chemical state information.
  2. It is possible to focus X-rays into a small spot using the monochromator. This means that small area XPS can be conducted with high sensitivity.



Comparison of the spectra obtained from:

(1) a diffraction grating by diffraction and

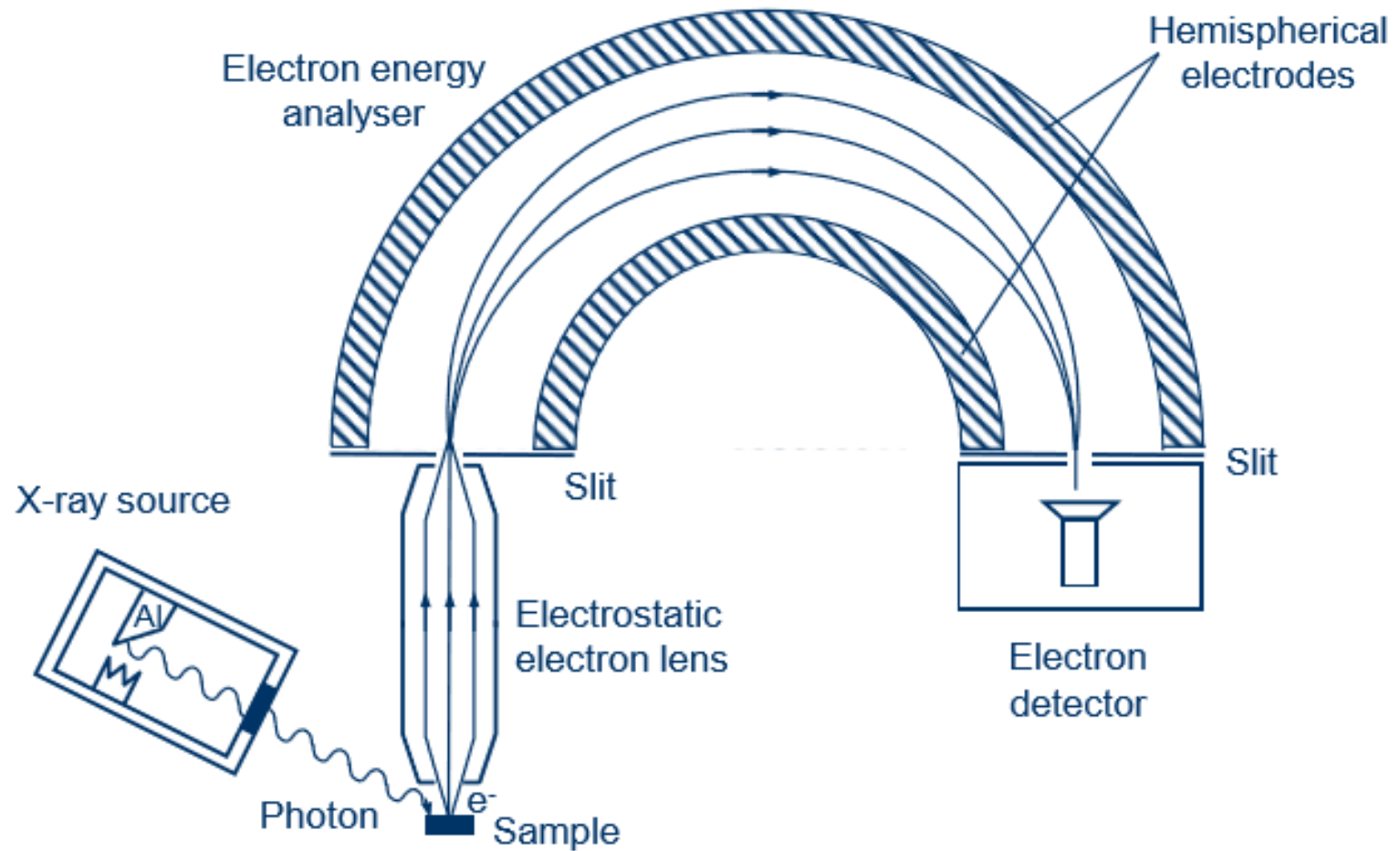
(2) a prism by refraction.

Longer wavelengths (red) are diffracted more, but refracted less than shorter wavelengths (violet).

## Analysers for Electron Spectroscopy:

- Commonly used electron energy analyzer in XPS is the **concentric hemispherical analyzer** (CHA).
- Here the electrons ejected from the sample are **collimated** into a beam by a slit in the chamber and then they can be **sorted** into their velocities by a magnetic field.
- The path of moving electrons is curved into a circle whose **radius is directly proportional to their velocity and inversely proportional to the magnitude of the field**, so that increasing the field from zero cause electrons of successively higher velocities to be recorded by the detector.
- Between the sample and the analyzer there is usually **a lens, or a series of lenses**.
- The **kinetic energy** of the electrons as they are ejected from the sample is usually **too great** for the analyzer to produce sufficiently high resolution so they **must be retarded**. This retardation is achieved either within the lens or, using parallel grids, between the lens and the analyser.





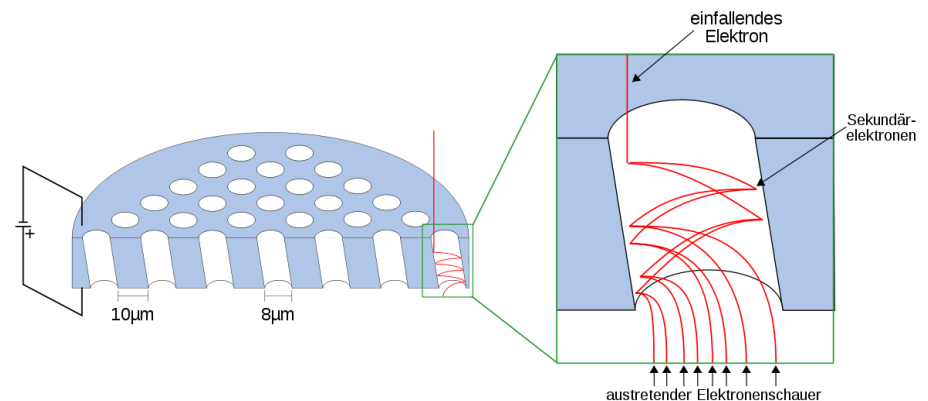
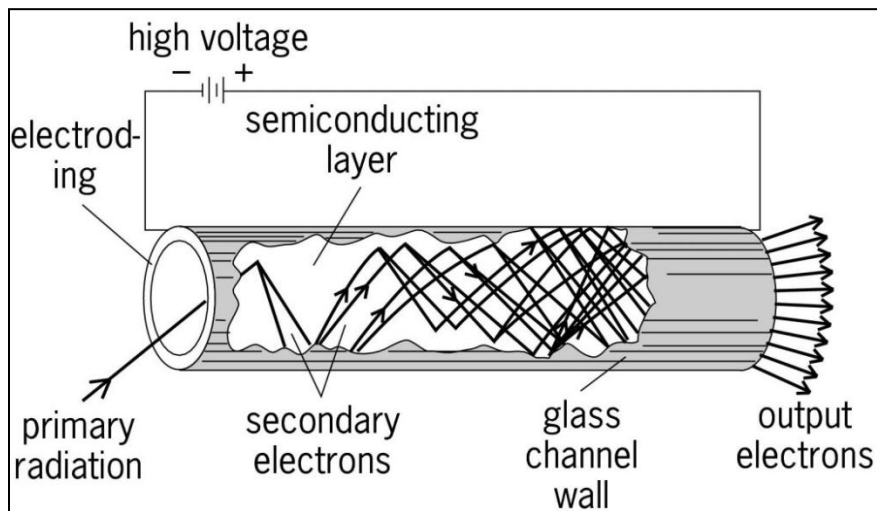
Number of emitted electrons measured  
as function of their kinetic energy

## Analysers for Electron Spectroscopy:

- A hemispherical analyzer can be operated in two modes, namely, Constant Analyzer Transmission **(CAT)** or Constant Retard Ratio **(CRR)**.
- In CAT mode, the **pass energy of the analyzer is held at a constant** value and it is **entirely the job of the transfer lens system** to retard the given kinetic energy channel to the range accepted by the analyzer.
- Most XPS spectra are acquired using CAT.
- The alternative mode, CRR, **scans the lens system but also adjusts the analyzer pass energy** to maintain a constant value for the quantity “initial electron energy”.

# Detectors

- In most electron spectrometers it is necessary to **count the individual electrons** arriving at the detector.
- To achieve this, **electron multipliers** are used.
- Although there are many types of electron multiplier, only two types are **commonly used** in electron spectrometers: **channel electron multipliers** (channeltrons) and **channel plates**.



## Advantages of XPS or ESCA Analysis

If surface chemistry or thickness is critical to product function and safety, XPS analysis is a proven choice. It provides a detailed breakdown of the elemental composition (at the parts per thousand range), empirical formula, chemical state, and electronic state of the elements contained in the material's surface. The following are the top reasons to consider XPS as a materials test for your product sample.

### 1. XPS analysis is effective across a range of organic and inorganic materials.

XPS can detect all elements except hydrogen and helium, with detection limits of ca. 0.1 atomic percent. This makes it an ideal analysis for both conductive and insulating samples including ceramics, glasses, polymers, semiconductors, metals, composite materials, and strongly adsorbed liquids or gases on surfaces.

### 2. XPS is a leading technique for analyzing [stainless steel passivation](#).

For any industry that leverages stainless steel for manufacturing or within manufacturing processes, rust prevention is a top priority to ensure products or equipment are quality-made, safe, and function as intended. XPS checks a material's corrosion, adhesion, and friction properties, as well as any chemical reactions to ensure it's up to the challenge.

### 3. XPS is also effective at identifying surface contaminants.

The XPS process can distinguish contaminants or stains present on the thin surface layers of plastics or polymers, providing data that may lead to the source of the problem within the manufacturing process. Furthermore, if suspect metal inter diffusion is an issue, XPS can provide the empirical formula of a material that is free of excessive surface contamination.

### 4. XPS is an efficient testing method.

When you work with an [experienced materials processing lab](#), analysis can be done in as little as 30 minutes with full results within one business day.

## Disadvantages of ESCA or XPS Analysis

While very versatile, XPS is not a good choice for all materials testing. These are a few of the reasons why you may wish you consider [other types of materials testing](#).

### 1. Size matters.

The sample cannot exceed 1 inch (25 mm) in any lateral direction, and height should not exceed ½ inch (12 mm).

It's also important to note that size can be a limiting factor depending on the sample. Cutting a sample is not always an option and can lead to added contamination of the area of interest.

### 2. Challenges with reproducibility.

Similar to other surface analysis techniques, XPS is associated with a 10% relative error in repeated analyses. In addition, the measured or inferred value and its actual value may differ by up to 20%.

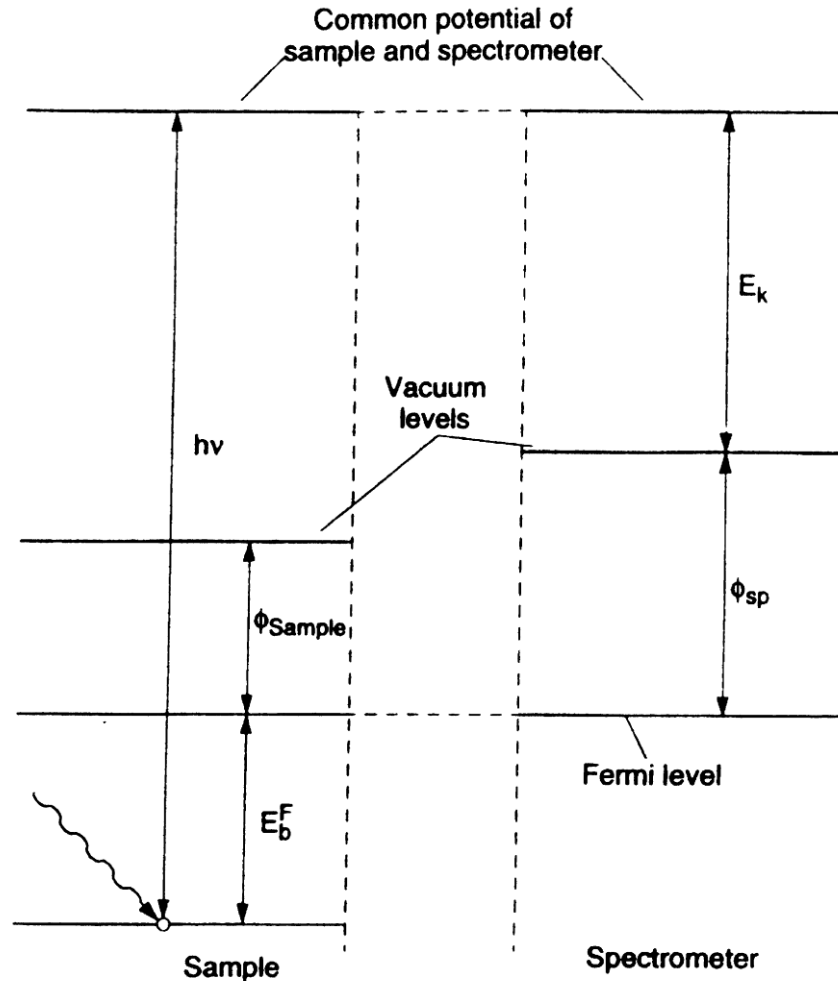
### 3. Samples must be compatible with high vacuum environment.

Samples must be amenable to a high vacuum environment (ca.  $1 \times 10^{-9}$  Torr). So, if your sample will outgas when placed under vacuum, XPS is not the right test for your needs.

**Why is the work function of the sample is not considered to formula for the kinetic energy of the photoelectron, whereas the work function of detector does get considered?**

The short answer to this question is twofold (i) we calibrate the binding energy scale with respect to the Fermi level and (ii) the kinetic energy of the photoelectrons is measured by the spectrometer.

Please see the attached image:



Cont.

1. The electron in one of the energy levels of the sample is kicked out by a photon of energy  $h\nu$  (the left side of the image).
2. The electron (now it is appropriate to call it a photoelectron) travels in vacuum to the spectrometer (middle part of the image).
3. The kinetic energy of the photoelectron is measured by the spectrometer as  $E_k$  (the right side of the image).

Now if you look at the "length" of the arrows in the image you can see that

$$h\nu = E_k + \phi_{sp} + E_B^F$$

Because the binding energy is almost always scaled to the Fermi level then it is very common to drop the superscript F and write

$$h\nu = E_k + \phi_{sp} + E_B$$

There you have it; the binding energy of the photoelectron depends on the work function of the spectrometer ( $\phi_{sp}$ ) not the sample ( $\phi_{sample}$ ).

There is one thing to keep in mind here, that is, this is valid only for the case where the sample is metal (or better to say sufficiently conductive) and the sample and spectrometer are in Ohmic contact, which causes their Fermi levels to align.