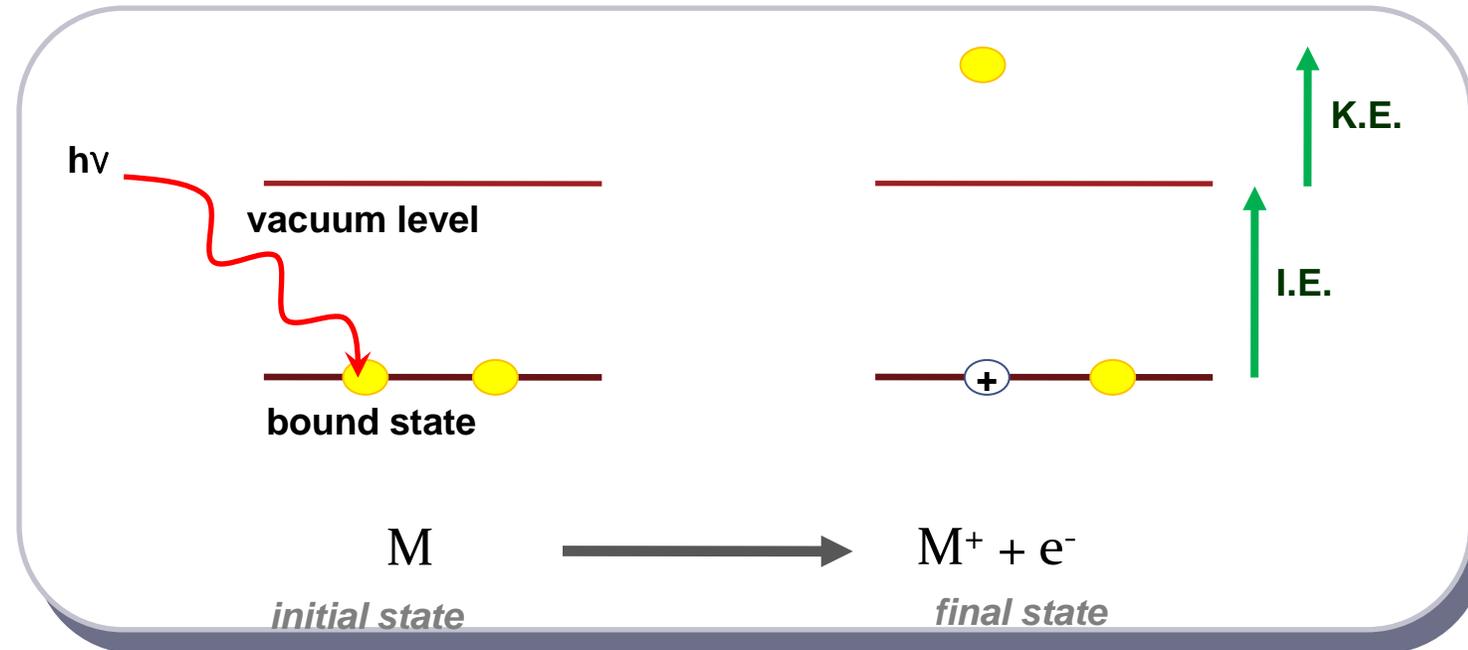


ESCA(Electron Spectroscopy for Chemical Analysis) or **XPS**(X-ray photoelectron spectroscopy)

- XPS is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material.
- XPS spectra are obtained by irradiating a material with a beam of Al or Mg X-rays while simultaneously measuring the kinetic energy (KE) and number of electrons that escape from the top 1 to 10 nm of the material being analyzed.
- XPS detects elements with an atomic number (Z) between those of Li ($Z=3$) and Lr ($Z=103$).

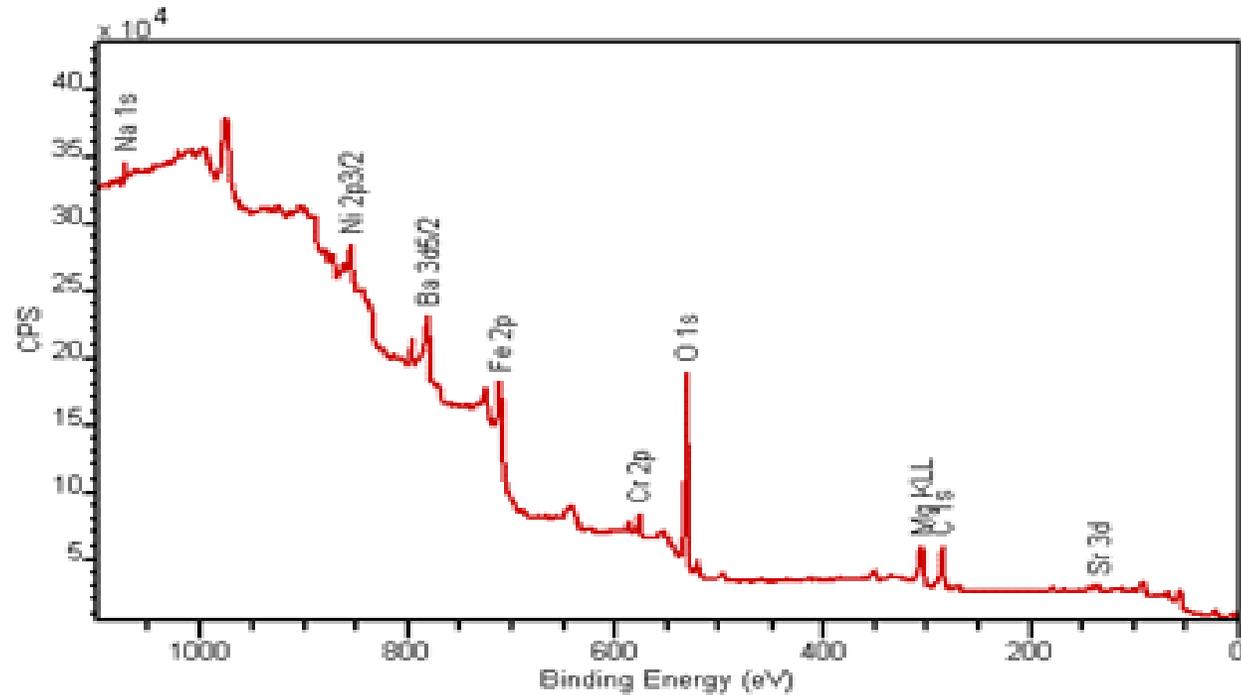
Detection Process



➤ Kinetic energy of emitted electron (E_k) is measured in an electron spectrometer

- Binding energy (E_b) of the electron can be determined using the equation of $E_b = h\nu - E_k - w$

XPS survey spectrum



- ✓ Binding Energy of an electron is depending on the **atomic orbital**, which the electron was emitted

Working Processes

➤ Primary Processes

1) Photoionization



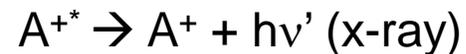
$$E \text{ (kinetic)} = E \text{ (photon)} - E \text{ (binding)}$$

2) Electron Ionization



➤ Secondary Processes :

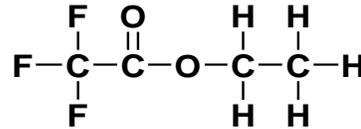
3) Photon Emission



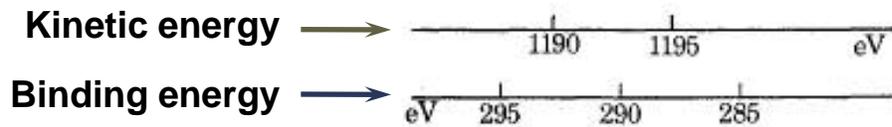
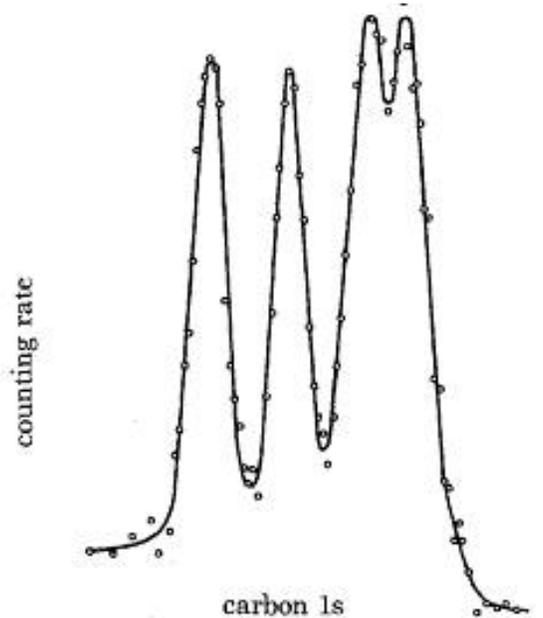
4) Auger Electron Emission



Chemical Shifts and Oxidation States



➤ *Electron spectrum from carbon 1s in ethyl trifluoroacetate*

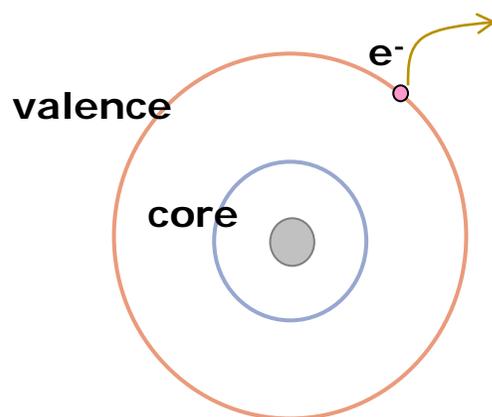


- ✓ *Binding energy increases as a function of **electronegativity***
- ✓ *Similar effects observed for different **oxidation states***

Chemical Shifts and Oxidation States

	Oxidation state	S	Se	Te
X^{-2}	-2	-1.4	-0.8	-0.6
X^0	0	0	0	0
XO_3^{-2}	+4	3.6	3.7	2.9
XO_4^{-2}	+6	5.5	4.2	3.6

ΔE_b



➤ **Oxidation** : valence electron density ↓

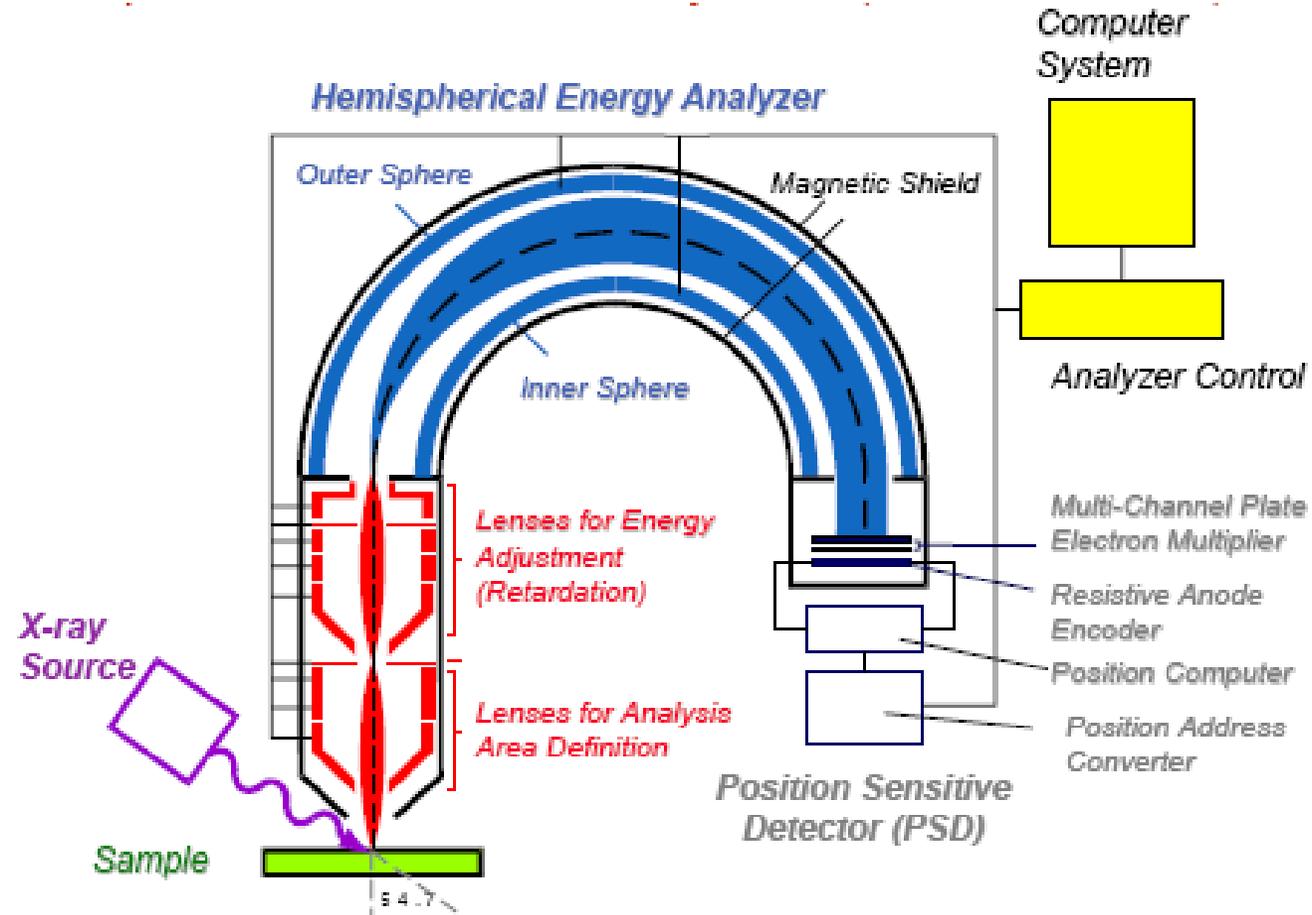
⇒ nuclear pot. ↑ ⇒ repulsive pot. ↓

⇒ binding energy ↑

Instrument Components

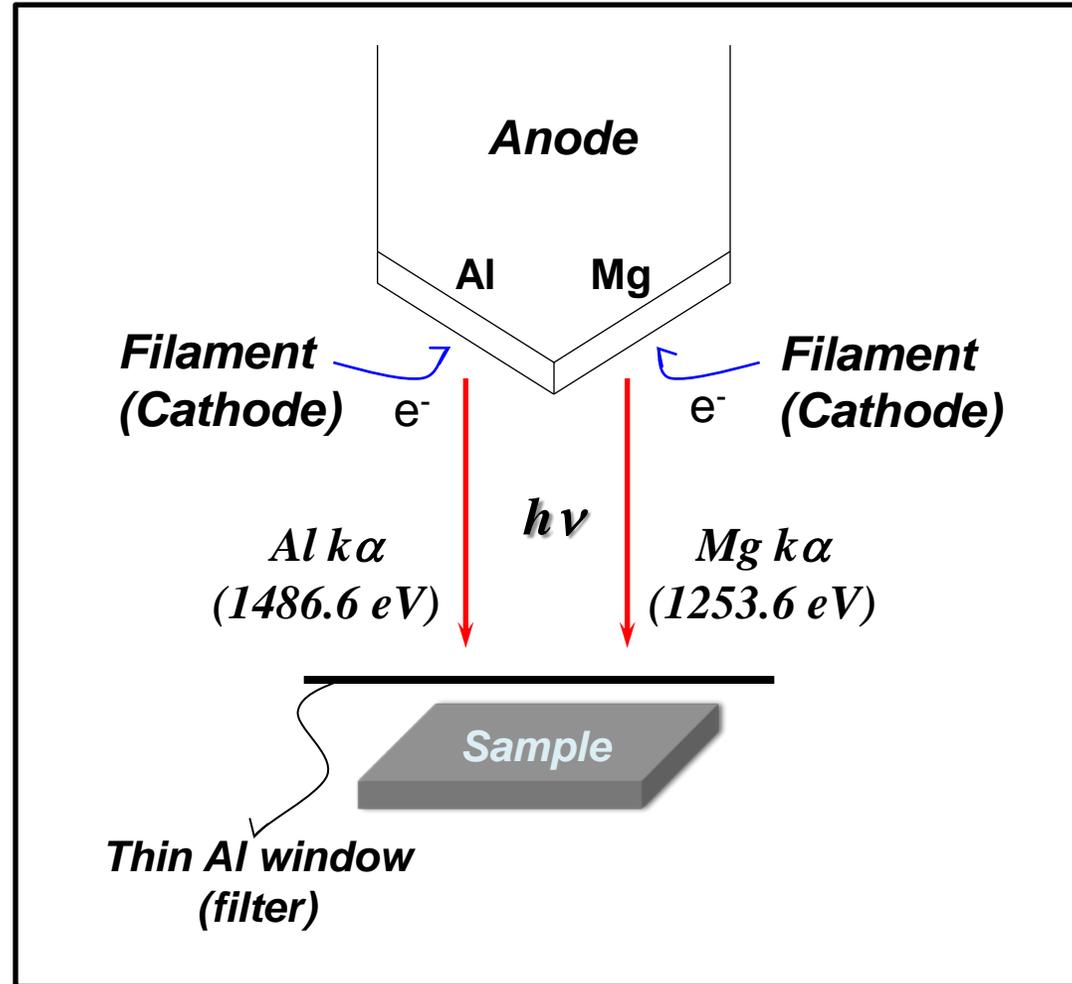
- A source of X-rays
- An ultra-high vacuum (UHV) stainless steel chamber with UHV pumps
- An electron collection lens
- An electron energy analyzer
- An electron detector system
- A moderate vacuum sample introduction chamber
- Sample mounts
- A sample stage
- A set of stage manipulators

Scheme of instrument



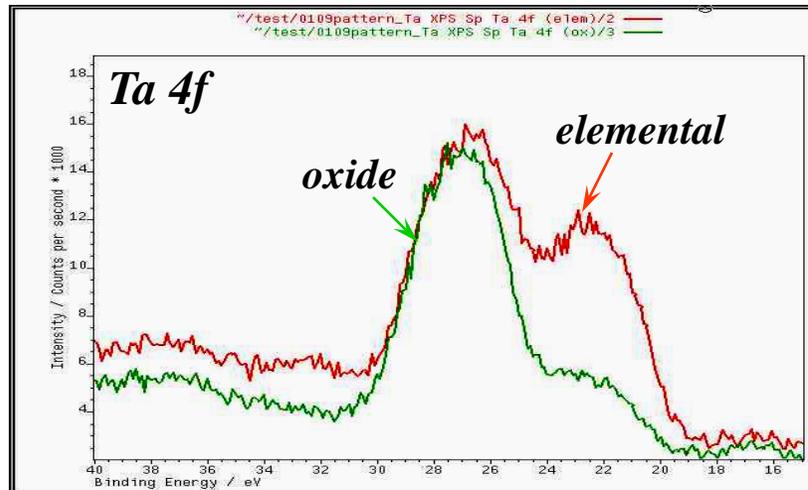
- Requires ultra high vacuum systems (10^{-5} to 10^{-10} torr)

Source of XPS



Mapping

*Imaged using
oxide signal*



*Imaged using
elemental signal*

