XPS/X-ray Photoelectron Spectroscopy (ESCA)

XPS gives information about atomic composition, structure and oxidation state of the compounds.



<u>Principle:</u> X-ray of certain energy, hv, displaces electron from the inner shell of binding energy, Eb; kinetic energy of emitted electron is measured by spectrometer. From this, binding energy, which is characteristic of the atom and orbital, is calculated.

w: work function of spectrometer (correction for electrostatic environment)

<u>XPS spectrum</u>: The spectrum consists of number of emitted electrons as a function of the energy.



On the picture XPS spectrum of organic compound is represented

• No peak for H (elements starting only from Li can be determined by XPS): very small diameter of the atom reduces electron catching probability to almost zero.

• Additional peak for O is present due to surface oxidation of the sample.

• Auger electrons' peaks can be present on XPS spectra. To distinguish these from XPS peaks, incident beam of different energy is tried, Auger peak will remain unchanged.

• 1s orbitals electrons' $\mathsf{E}_{\mathsf{bin}}$ increases with increase of atomic number because of increased positive charge of the

nucleus.

• More than one peak can be present for one element, e.g. peaks for both 2s and 2p orbitals for S and P in the spectrum.

Oxidation state and structure determination:

When peak is examined under the condition of higher energy resolution, position of the peak depends to a small degree on a chemical environment of the atom.

- Presence of outer electrons diminishes the attraction of the nucleus for core electrons. When one of these
 electrons is removed the effective charge sensed for core electrons increases, so increases the binding
 energy. To conclude, as the oxidation state of specie increases, E_{bin} also increases.
- Structure is determined by taking in account the effect of functional groups on the effective nuclear charge experienced by the atom of interest. In a compound with different functional groups, those with higher electron withdrawing ability reduce the nuclear charge of the atom to which they are bonded. Therefore, these atoms have higher binding energy than others.

<u>Spectrometer</u>: Spectrometers may have different design, some are modified only for XPS analysis, and some have also Auger and UPS measurement modes.

- Source: monochromatic X-ray beam can be produced by X-ray tube equipped with Al or Mg targets, synchrotron or crystal monochromator.
- Sample holders: sample holder should be positioned to the closest position to source and analyzer. In order to prevent attenuation of the beam on the surface and avoid surface contamination by oxygen and/or water sample compartment should be evacuated.
- Analyzers: generally hemispherical type analyzers are employed. There, the electron beam is deflected by an electromagnetic field in such a way that electrons travel a curved path. The radius of curve depends on E_{kin} of electrons and magnitude of the field. By varying field strength electrons of different E_{kin} can be analyzed.

• Transducers are usually based on solid state channel electron multiplier consisting of glass tubes doped with Pb or V.

References:

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