X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

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INTRODUCTION TO X-RAY PHOTOELECTRONS SPECTROSCOPY
What is XPS? General Theory

How can we identify elements and compounds?

What is the instrumentation of XPS?
X-ray Photoelectron Spectroscopy (XPS) is also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a widely used technique to investigate the chemical composition of surfaces.
1. In 1887, Henriech Rudolf Hertz, photoelectric effect

2. In 1907, Innes the first XPS spectrum

3. Kai Siegbahn (Uppsala) with Hewlett Packard (USA) produce the first commercial monochromatic XPS
PHOTOELECTRIC EFFECT

- Photons
- Electrons Ejected from the Surface
- Sodium Metal
Following this process, the atom will release energy by the emission of an Auger Electron.
AUGER RELATION OF CORE HOLE

Conduction Band

Valence Band

Fermi Level

Free Electron Level

Emitted Auger Electron

1s
2s
2p
L1
L2, L3
K
XPS is used for:

- What elements and the quantity elements of the sample surface (1-12nm)
- What contamination in the surface or the bulk of the sample
- Empirical formula of a material
- The chemical state identification of the elements in the sample
- The binding energy of electronic states
- The thickness of different materials
- The density of electronic state
INSTRUMENTATION FOR
X-RAY PHOTOELECTRON
SPECTROSCOPY
COMPONENTS OF XPS:

- A source of X-rays
- An ultra high vacuum (UHV)
- An electron energy analyzer
- Magnetic field shielding
- An electron detector system
- A set of stage manipulators
XPS Instrument

- X-Ray Source
- Ion Source
- SIMS Analyzer
- Sample introduction Chamber
X-RAY PHOTOELECTRON SPECTROMETER

- **Electron Optics**
- **X-ray Source**
- **Sample**
- **Hemispherical Energy Analyzer**
  - Outer Sphere
  - Magnetic Shield
  - Inner Sphere
- **Position Sensitive Detector (PSD)**
- **Computer System**
- **Analyzer Control**
  - Multi-Channel Plate Electron Multiplier
  - Resistive Anode Encoder
  - Position Computer
  - Position Address Converter

- Lenses for Energy Adjustment (Retardation)
- Lenses for Analysis Area Definition
X-RAY GENERATION

Incident electron

Conduction Band

Valence Band

Secondar y electron

Conduction Band

Valence Band

Free Electron Level

Fermi Level

1s

2s

2p

X-ray Photon

X-ray Photon

L1

L2, L3

K

Photon
Relative Probabilities of Relaxation of a K Shell Core Hole

Note: The light elements have a low cross section for X-ray emission.
WHY WE USE UHV?

- Remove adsorbed gases from the sample.
- Eliminate adsorption of contaminants on the sample.
- Prevent arcing and high voltage breakdown.
- Increase the mean free path for electrons, ions and photons.
A monoenergetic x-ray beam emits photoelectrons from the surface of the sample.

Ultra-high vacuum environment to eliminate excessive surface contamination.

The x-ray photons penetrate about a micrometer of the sample.

Cylindrical Mirror Analyzer (CMA) measures the KE of emitted e- s.

The XPS spectrum contains information only about the top 10 - 100 Å of the sample.

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.
XPS is routinely used to analyze inorganic compounds, metals, semiconductors, polymers, ceramics, etc.

Organic chemicals are not routinely analyzed by XPS because they are readily degraded by either the energy of the X-rays or the heat from non-monochromatic X-ray sources.
XPS detects all elements with (Z) > 3. It cannot detect H (Z = 1) or He (Z = 2) because the diameter of these orbitals is so small, reducing the catch probability to almost zero.

Dedection unit: ppt and some conditions ppm
For example: determination of aluminum oxide thickness with XPS.
APPLICATIONS OF X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)
XPS analysis showed that the pigment used on the mummy wrapping was Pb$_3$O$_4$ rather than Fe$_2$O$_3$. 

Egyptian Mummy
2nd Century AD
World Heritage Museum
University of Illinois
Woven carbon fiber composite

XPS analysis identifies the functional groups present on composite surface. Chemical nature of fiber-polymer interface will influence its properties.
XPS devices is also named ESCA (Electron Spectroscopy Chemical Analysis). It works base on the photoelectron effect.

XPS is primarily used for chemical analysis as determining thicknesses and empirical formulas of different elements and binding energies, densities of electronic states.

XPS is used from starting Li(A≥3) because of smaller orbital’s radius and analysis of organic compounds cannot be done with XPS because of degradation with radiation.

XPS is used also determination of others like; metals, ceramics, semiconductors, papers, etc.
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