PHOTOELECTRON SPECTROSCOPY (XPS)

PRINCIPLES AND APPLICATIONS

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Photoelectron Spectroscopy XPS

• What is XPS?
• Aim of XPS Analysis.
• General Theory
• How can we identify elements and compounds?
• Instrumentation for XPS
• Examples of materials analysis with XPS
What is XPS?

- X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a widely used technique to investigate the chemical composition of surfaces.
- Sample is illuminated with soft (1.5kV) X-ray radiation in an ultrahigh vacuum.
- The photoelectric effect leads to the production of photoelectrons, the energy spectrum of which can be determined in a beta-ray spectrometer.

_X-ray Photoelectron spectroscopy, based on the photoelectric effect_,

1, 2 was developed in the mid-1960’s by Kai Siegbahn and his research group at the University of Uppsala, Sweden. 3

The Atom and the X-Ray

Core electrons

Valence electrons

Free electron

X-Ray

The core electrons respond very well to the X-Ray energy

X-Rays on the Surface

e⁻ top layer

e⁻ lower layer

with collisions

e⁻ lower layer

but no collisions

X-Rays

Atoms layers

Outer surface

Inner surface
X-Rays on the Surface

• The X-Rays will penetrate to the core $e^-$ of the atoms in the sample.

• Some $e^-$s are going to be released without any problem giving the Kinetic Energies (KE) characteristic of their elements.

• Other $e^-$s will come from inner layers and collide with other $e^-$s of upper layers
  – These $e^-$ will be lower in lower energy.
  – They will contribute to the noise signal of the spectrum.

X-Rays and the Electrons

The noise signal comes from the electrons that collide with other electrons of different layers. The collisions cause a decrease in energy of the electron and it no longer will contribute to the characteristic energy of the element.
Aim of XPS Analysis

- Identification of elements at surfaces (depth: 10 nm).
- Identification of functional groups and redox states.
- Concentration and depth profiling.
- Estimation of over layer thickness.
- Comparison of bulk and surface composition.
- Surface homogeneity/heterogeneity
- Possible surface morphology of adlayers.

Physical Bases

- Based upon photon in/electron out process.
- Photon E (Einstein ): \( E = h\nu \)

where: \( h \) - Planck constant (6.62 x 10\(^{-34}\) J s).
\( \nu \) - frequency (Hz) of the radiation.

- In XPS the photon is absorbed by an atom in a molecule or solid, leading to ionization and the emission of a core (inner shell) electron.
- If the photon interacts with valence levels (ionization by lost of one of them) the technique is different and called UPS, Ultraviolet photoelectron spectroscopy.
Photoelectric effect

What is photoemission?

Photon in $\rightarrow$ electron out (emission)
Introduction to the Solid State

In solids, atomic and molecular energy levels broaden into bands that in principle contain as many states as there are atoms/molecules in the solid.

Process of Photoionization

\[ A + h\nu \rightarrow A^+ + e^- \]

\[ E(A) + h\nu = E(A^+) + E(e^-) \]

\[ KE = h\nu - [ E(A^+) - E(A) ] \]

• The difference in energy between the ionized and neutral atoms, is generally called the **binding energy** (BE) of the electron:

\[ KE = h\nu - BE \]
XPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).

The ejected photoelectron has kinetic energy:

\[ KE = h\nu - BE - \phi \]

Following this process, the atom will release energy by the emission of an Auger Electron.
The BE is a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level and the KE of the photoelectron is again given by:

\[ KE = h\nu - BE \]

NOTE - the binding energies (BE) of energy levels in solids are conventionally measured with respect to the Fermi-level of the solid, rather than the vacuum level.

This involves a small correction to the equation given above in order to account for the work function (\(\phi\)) of the solid, but for the purposes of the discussion below this correction will be neglected.

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**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.

This is the point with 0 energy of attraction between the electron and the nucleus. At this point the electron is free from the atom.

These electrons are attracted to the proton with certain binding energy \(x\).
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-s are local close to the nucleus and have binding energies characteristic of their particular element.
- The core e-s have a higher probability of matching the energies of AlKα and MgKα X rays.

XPS Spectra

1- Characteristic binding energy associated with each core atomic orbital i.e. each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies.

2- The presence of peaks at particular energies therefore indicates the presence of a specific element in the sample under study.

3- The intensity of the peaks is related to the concentration of the element within the sampled region. (quantitative analysis of the surface composition).
KE versus BE

KE can be plotted depending on BE.

Each peak represents the amount of e's at a certain energy that is characteristic of some element.

BE increase from right to left

KE increase from left to right

XPS Spectrum

• The XPS peaks are sharp.

• In a XPS graph it is possible to see Auger electron peaks.

• The Auger peaks are usually wider peaks in a XPS spectrum.

• Aluminum foil is used as an example on the next slide.
Identification of XPS Peaks

- The plot has characteristic peaks for each element found in the surface of the sample.

- There are tables with the KE and BE already assigned to each element.

- After the spectrum is plotted you can look for the designated value of the peak energy from the graph and find the element present on the surface.
X-rays vs. e⁻ Beam

- **X-Rays**
  - Hit all sample area simultaneously permitting data acquisition that will give an idea of the average composition of the whole surface.

- **Electron Beam**
  - It can be focused on a particular area of the sample to determine the composition of selected areas of the sample 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
How Does XPS Technology Work?

• A monoenergetic x-ray beam emits photoelectrons from the surface of the sample.

• The penetration of the x-ray photons 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.

• Cylindrical Mirror Analyzer (CMA) or hemispherical sector analyzer (HSA) measure the KE of emitted e-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.

Instrumentation:
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
The basic requirements:

• A source of fixed-energy radiation (an x-ray source).

• An electron energy analyzer (which can disperse the emitted electrons according to their kinetic energy, and thereby measure the flux of emitted electrons of a particular energy).

• A high vacuum environment (to enable the emitted photoelectrons to be analyzed without interference from gas phase collisions).
X-ray Photoelectron Spectrometer

Diagram of the Side View of XPS System
Schematic Diagram of XPS

Energy of Light

<table>
<thead>
<tr>
<th>Wavelength ($\lambda$)</th>
<th>Energy (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^6 \mu m$</td>
<td>$10^6 eV$</td>
</tr>
<tr>
<td>$10^3 \mu m$</td>
<td>$10^3 eV$</td>
</tr>
<tr>
<td>$1 \mu m$</td>
<td>$1 eV$</td>
</tr>
<tr>
<td>$10^{-3} \mu m$</td>
<td>$1 KeV$</td>
</tr>
<tr>
<td>$10^{-6} \mu m$</td>
<td>$1 MeV$</td>
</tr>
</tbody>
</table>

Radiations:
- Broadcast
- Short wave radio
- Infrared
- Visible
- UV
- X-ray
- Gamma Ray
**X-Ray Sources**

- 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.
- 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.
- The X-Ray source produces photons with certain energies:
  - MgK$\alpha$ photon with an energy: $h\nu = 1253.6$ eV
  - AlK$\alpha$ photon with an energy: $h\nu = 1486.6$ eV

The emitted photoelectrons will therefore have kinetic energies in the range of ca. 0 - 1250 eV or 0 - 1480 eV

**X-ray Source Requirements**

- 1. High X-ray flux at sample
- 2. Narrow X-ray line width
- 3. Multiple-anode capability
- 4. Ability to move the X-ray source (X-Y) and retract it (Z)
- 5. Long anode and filament lifetime
**The X-ray source for XPS:**

- In contrast to the electron source, the X-ray source energy depends on the choice of the anode material, resulting in the availability of a number of discrete energies rather than a continuous variation of the energy, as exists for electron and ion guns.
- The photon energy must be sufficiently high to excite intense photoelectron peaks from all elements of the periodic table.
- For XPS analysis, it is very important to consider the energy resolution of the primary X-rays.

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**X-ray tube**

*Early x-ray source*

*Standard lab X-ray source is by very high energy electron beam hitting the anode.*
X-ray spectrum from x-ray tube

Characteristic lines from the X-ray fluorescence process (XRF) and a broad background (Bremsstrahlung), which is strongly depends on the energy of the electron.

Monochromatic X-ray

Goal to achieve

1. Narrow peak width
2. Reduced background
3. No satellite & Ghost peaks

**Quartz**

Crystal Disperser

\[ n\lambda = 2d\sin\theta \]

For quartz (1010) surface, \( d = 0.42 \text{ nm} \) and 78.5 degree for Al K\( _\alpha \) 0.93 nm.
Synchrotron Radiation

The synchrotron storage ring is a tubular vacuum chamber made to:

Hold an electron beam travelling through it at nearly the speed of light. Maintain the high energy of the electron beam. As the accelerating electrons circle the ring at relativistic velocities, they give off intense beams of light including x-rays. By using a monochromator the light will be **Monochromatic**.

Key properties of synchrotron radiation:
- high intensity
- tunability in wide range
- near-coherence
- polarized.
- pulsed
- well collimated

NUS has such a source in Singapore!

Sample charging effects

The light for XPS always charges surface positively (shifting of spectrum to higher binding energy) and leads to general instability (spectral noise).

For the metal sample, which can be grounded and the charges can be quickly gone.

However, for insulator, this effects are serious and need to be treated.

For XPS (even AES) never forget ground the sample !!!

C 1s shifts due to the charging
Inhomogeneous Surface Charging

Charging can even change the line shape due to Inhomogeneous Surface Charging, which have different positive voltage on the surface.

In a lot of cases, there is only spectral shift due to charging, which can be determined by comparison with known elemental XPS lines, for example C 1s.

Vacuum System

- The instrument uses different pump systems to reach the goal of an Ultra High Vacuum (UHV) environment.
- The Ultra High Vacuum environment will prevent contamination of the surface and aid an accurate analysis of the sample.
UHV for Surface Analysis? Why

- 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.

XPS Analyzer

Analyzer Requirements

1. Precision energy measurement across a wide energy range
2. High-energy resolution capability
3. Ability to define the analysis area and, if possible, to change it
4. High dynamic range and low noise detector
Instrumentation (analyzers)

Analyzer:

Most essential part of any electron spectroscopy, its characteristic are: energy range, energy resolution, sensitivity and acceptance angle.

Normally its functions involve: retarding of the incoming electron, selection of the electrons with right kinetic energy (pass energy), detecting of the electrons (channeltron)

Detection of electron energy (Analyzers)

• Mainly two types of detectors are used in AES and XPS systems: The cylindrical mirror analyser (CMA) and the hemispherical sector analyzer (HSA).
• In the past, the CMA was preferred for AES systems merely for geometrical reasons and for its high analyzer transmission function, and the HSA analyzer for XPS for its superior energy resolution.
• More and more, however, depending on the constructor and on the requirements of the customer, the HSA detector is also used in AES systems.
• A multifunctional AES-XPS system is evidently operated by only one electron detector, and mostly a HSA type is chosen.
• Yet, it is important to mention that not all of the requirements imposed by the type of analysis coincide for XPS and AES.
The hemispherical sector analyzers (HSA)

- All constructors use HSA detectors for electron dispersion analysis in XPS.
- A typical configuration is shown in Fig. bellow.
- The HSA is designed to have a constant and as high as possible energy resolution for the detection of photoelectrons.
- The best energy resolution in XPS is 0.4 eV, corresponding to the linewidth of the monochromator.
- In order to reduce the size of the analyzer, it is standard practice to retard the kinetic energies of the photoelectrons either to a user-selected analyzer energy, called pass energy, or by a user-selected ratio.

Mode of fixed analyzer transmission mode (FAT)

- Also known as the constant analyzer energy mode (CAE).
- In this mode of operation, which is applied for the detection of photoelectrons, a constant voltage is applied across the hemispheres allowing electrons of a particular energy to pass between them.
- The most important characteristic in this case is a constant energy resolution in the spectrum as a function of the energy, in contrast to the CMA analyser where a relative energy resolution is obtained.
- The electrons are emitted from the specimen and transferred to the focal point of the analyzer by the lens assembly.
- At this point they are retarded electrostatically before entering the analyzer itself.
- Those electrons with energies matching the pass energy of the analyser are transmitted, detected and counted by the electron detector.
- The retarding field potential is then ramped, and so the electrons are counted as function of energy.
Improving Sensitivity of HSA

- To improve the sensitivity of the HSA, the electron detection is done by a multichannel detector system.
- Depending on the type of system, the number of electron multipliers may go up to 16.
- This parallel electron detection is especially useful when a monochromator is used due to the loss of intensity of the primary X-rays.
Sample Preparation & Surface Damage in XPS

1. Any sample that is vacuum stable can be analyzed by XPS.

2. Sample containing volatile components can be cooled to low temp. to avoid devolatilization.

3. Normally, solid materials, such as metals, ceramics & polymer, are fairly stable under X-ray irradiation and damage caused by X-ray is minimal during a typical XPS experiment.

4. Films, plaques or powders can be mounted on a sample holder with a double-sided sticky tape of low volatility first and then examined as bulk samples.

5. Certain Polymer & Biological samples would undergo some chemical changes under prolonged X-ray exposures in an XPS experiment. Examples are: PTFE, PVC, PVA, especially, when the materials are in thin films.

6. To minimize the damage, the exposure time should be as short as possible, and the samples are cooled to low temperatures.

7. The causes for the XPS induced damage include: secondary electrons generated at X-ray source & impinging on the polymer or biological sample surface.
XPS Instrument

The XPS is controlled by using a computer system.

The computer system will control the X-Ray type and prepare the instrument for analysis.

University of Texas at El Paso, Physics Department
Front view of the Phi 560 XPS/AES/SIMS UHV System and the computer system that controls the XPS.

Where do Binding Energy Shifts Come From? Or element or compound identification.
Elemental Shifts

<table>
<thead>
<tr>
<th>Element</th>
<th>2p&lt;sub&gt;3/2&lt;/sub&gt;</th>
<th>3p</th>
<th>△</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>707</td>
<td>53</td>
<td>654</td>
</tr>
<tr>
<td>Co</td>
<td>778</td>
<td>60</td>
<td>718</td>
</tr>
<tr>
<td>Ni</td>
<td>853</td>
<td>67</td>
<td>786</td>
</tr>
<tr>
<td>Cu</td>
<td>933</td>
<td>75</td>
<td>858</td>
</tr>
<tr>
<td>Zn</td>
<td>1022</td>
<td>89</td>
<td>933</td>
</tr>
</tbody>
</table>

Electron-nucleus attraction helps us identify the elements.
Binding Energy Determination

The photoelectron’s binding energy will be based on the element’s final-state configuration.

<table>
<thead>
<tr>
<th>Initial State</th>
<th>Free Electron Level</th>
<th>Final State</th>
<th>Conduction Band</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conduction Band</td>
<td>Valence Band</td>
<td>Conduction Band</td>
<td></td>
</tr>
<tr>
<td>1s</td>
<td>2s</td>
<td>2p</td>
<td></td>
</tr>
</tbody>
</table>

Electronic Effect

Spin-Orbit Splitting or Spin-Orbit Coupling

- Some electronic levels (most obviously 3p and 3d) give rise to a closely spaced doublet, which appear when spectra expanded.
- Permitted J values = L ± S
- Coupling between L: The Angular Q.N., S: Unpaired Spin
- The lowest energy final state is the one with maximum J
- The relative intensities of the two peaks reflects the degeneracies of the final states (\(gJ = 2J + 1\)),
  - \(^2D\ 5/2\): \(gJ = 2\times(5/2) + 1 = 6\) (lower B.E)
  - \(^2D\ 3/2\): \(gJ = 2\times(3/2) + 1 = 4\) (higher B.E)
- These two values determine the probability of transition to such a state during photoionization.
For p, d and f peaks, two peaks are observed.

The separation between the two peaks are named **spin orbital splitting.** The values of spin orbital splitting of a core level of an element in different compounds are nearly the same.

The **peak area ratios** of a core level of an element in different compounds are also nearly the same.

Spin orbital splitting and peak area ratios assist in element identifications.
s-Orbital

Orbital = s
l = 0
s = +/- 1/2
ls = 1/2

p-Orbital

Orbital = p
l = 1
s = +/- 1/2
ls = 1/2, 3/2
d-Orbital

Orbital = d
l = 2
s = +/- 1/2
ls = 3/2, 5/2

f-Orbital

Orbital = f
l = 3
s = +/- 1/2
ls = 5/2, 7/2
Chemical Shifts

The exact binding energy of an electron depends not only upon the level from which photoemission is occurring, but also upon:

1) The formal oxidation state of the atom.
2) The local chemical and physical environment.

Changes in either (1) or (2) give rise to small shifts in the peak positions in the spectrum - so-called chemical shifts.

Atoms of a higher positive oxidation state exhibit a higher binding energy due to the extra coulombic interaction between the photo-emitted electron and the ion core.

• The shifts are typically a few to 10 eV or more, and therefore detectors with a high energy resolution are used.
• To subtract chemical information, it is imperative to determine peak positions as accurately as possible.
• The line of interest is preferentially evoked by means of a monochromatic X-ray source, and recorded with the highest possible energy resolution.
• When dealing with small chemical shifts, overlapping peaks may anyway occur in the spectra.
• Peak deconvolution and peak fitting tools are available in the commercial data handling systems.
The capability to distinguish between different chemical states is the main characteristic of XPS.

Due to this, another acronym is in use for this technique: ESCA, which stands for 'Electron Spectroscopy for Chemical Analysis'.

FWHM: full width at half max. Int.
Why Chemical Shift In AES, the situation is less promising

- **Firstly**, most AES lines are by nature broader than XPS lines.
- **Secondly**, the Auger transition involves three electrons and the overall chemical shift is influenced by the three energy levels concerned.
  - In general, similar shifts of a few eV as for XPS are to be expected, especially when core electrons are involved in the transition.
  - Since in AES-specific equipment, detectors with lower energy resolution are used.
  - It is clear that chemical shifts in AES are not often measured accurately.
  - Moreover, peaks corresponding to transitions with valence electrons are broad and poorly defined, which makes the assignment of chemical shifts nearly impossible.
As the samples shown before, binding energies of Al$^{3+}$ is higher than the metal atom, in the meanwhile, the binding energy of O atom (more positive charge) is higher than the O$^{2-}$ ion.

**Chemical Shifts- Electronegativity Effects**

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrocarbon</td>
<td>C-H, C-C</td>
</tr>
<tr>
<td>amine</td>
<td>C-N</td>
</tr>
<tr>
<td>alcohol, ether</td>
<td>C-O-H, C-O-C</td>
</tr>
<tr>
<td>Cl bound to C</td>
<td>C-Cl</td>
</tr>
<tr>
<td>F bound to C</td>
<td>C-F</td>
</tr>
<tr>
<td>carbonyl</td>
<td>C=O</td>
</tr>
</tbody>
</table>

The chemical shifts due to the variation of the distribution of the charges at the atom site is the main reason for the other name of XPS: ESCA (Electron Spectroscopy for Chemical Analysis)
C1s envelope has been resolved into five components of polystyrene surface exposed to an oxygen plasma.
Final State Effects-Shake-up/ Shake-off

Results from energy made available in the relaxation of the final state configuration (due to a loss of the screening effect of the core level electron which underwent photoemission).

- **Monopole transition**: Only the principle quantum number changes. Spin and angular momentum cannot change.
- **Shake-up**: Relaxation energy used to excite electrons in valence levels to bound states (monopole excitation).
- **Shake-off**: Relaxation energy used to excite electrons in valence levels to unbound states (monopole ionization).

Figure 8. Examples of shake-up lines (e) of the copper 2p observed in copper compounds.
Shake-up and shake-off

Photoemission process can leave the ions in the ground state (main peak) and also possibly in an excited state (shake-up/shake-off satellites), the latter makes the KE of photoelectron less: higher BE.

- excitation of electron to bound state *shake-up satellite*.
- excitation of electron to unbound (continuum) state *shake-off satellite*.
- excitation of hole state *shake-down satellite* - rare.
The shown is XPS spectra for Cu 2p photoemission at different chemical states. The shake-up Lines does not exist in Cu metal, and is unique for CuO and CuSO₄.

**Energy loss lines**

\[ e_{ph} + e_{solid} \rightarrow e_{ph}^* + e_{solid}^{**} \]

Photoelectrons travelling through the solid can interact with other electrons in the material. These interactions can result in the photoelectron exciting an electronic transition, thus losing some of its energy (inelastic scattering). Most common are due to interband or plasmons (bulk or surface).
The plasmon loss satellites are rarely sharp in insulators but very prominent in the metals.

The main peak is normally observed at higher binding energy with several lines with the same energy intervals and reduced intensity, and the interval can be not only single one due to different origins: bulk or surface plasmons, bulk one is more prominent and interval larger ($2^{1/2}$ factor of the surface one).

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**Final State Effects - Multiplet Splitting**

*Following photoelectron emission, the remaining unpaired electron may couple with other unpaired electrons in the atom, resulting in an ion with several possible final state configurations with as many different energies. This produces a line which is split asymmetrically into several components.*
Relative Sensitivities of the Elements

XPS of Copper-Nickel alloy
Applications of X-ray Photoelectron Spectroscopy (XPS)

- 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.

Which Materials Analyzed
ANALYSIS OF XPS

- 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
**XPS Analysis of Pigment from Mummy Artwork**

**Artwork**

*Egyptian Mummy*
2nd Century AD
World Heritage Museum
University of Illinois

XPS analysis showed that the pigment used on the mummy wrapping was Pb$_3$O$_4$ rather than Pb$_2$O$_3$.

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**Analysis Carbon Fiber- Polymer Composite Material by XPS**

*XPS analysis identifies the functional groups present on composite surface. Chemical nature of fiber-polymer interface will influence its properties.*

*Woven carbon fiber composite*
Analysis of Materials for Solar Energy Collection by XPS Depth Profiling - The amorphous SiC/SnO /SnO$_2$ Interface

The profile indicates a reduction of the SnO$_2$ occurred at the interface during deposition. Such a reduction would effect the collector’s efficiency.

Data courtesy A. Nurrudin and J. Abelson, University of Illinois

Electron Spectroscopy for Chemical Analysis (ESCA)
a) The C1s spectrum (resolved into component peaks) for the hardsegment polyurethane;

(b) the O1s spectrum for the hard-segment polyurethane
(c) the N1s spectrum for the hard-segment polyurethane

X-rays will penetrate deeply into a sample, and stimulate electron emission throughout the specimen.

Only those electrons emitted from the surface zone that have suffered no energy loss will contribute to the photoemission peak.

Electrons emitted from the surface zone that have lost some energy due to inelastic interactions will contribute to the scattering background.
ESCA spectra are convolutions of the information from each depth within the sampling depth.

Figure 3.17 As the sample is rotated, maintaining the X-ray source and detector in fixed positions, the effective sampling depth decreases by a factor of \cos \theta. The sample angle, \theta, is defined relative to the normal to the surface.
Hydroxy groups and ethers on a surface cannot be distinguished based upon ESCA chemical shifts. If the surface is reacted with trifluoroacetic anhydride, only hydroxyl groups will pick up F. The size of the F peak in the ESCA spectrum will be proportional to the number of reacted hydroxyl groups.

**Case study of XPS**

**Compositional Analysis of Surfaces:**

Case I: Analysis of surface treatment of a piston.

Coating Material: Fluorocarbon
Polysiloxane Immobilized Ligand System

\[
\begin{align*}
\text{Polysiloxane Immobilized Ligand System} \\
\begin{array}{c}
\text{Reflux/Toluene} \\
\text{C}_2\text{H}_5\text{OH}
\end{array}
\end{align*}
\]
### XPS Results

<table>
<thead>
<tr>
<th>System</th>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>Core-line</td>
<td>285</td>
<td>102</td>
<td>532</td>
<td>399.5</td>
</tr>
<tr>
<td>%Composition</td>
<td></td>
<td>38.8</td>
<td>17</td>
<td>41.4</td>
<td>2.85</td>
</tr>
<tr>
<td>Product</td>
<td>Core-line</td>
<td>285</td>
<td>102</td>
<td>532</td>
<td>399.5</td>
</tr>
<tr>
<td>%Composition</td>
<td></td>
<td>42.4</td>
<td>19.3</td>
<td>28.7</td>
<td>9.6</td>
</tr>
</tbody>
</table>
Conclusion

• XPS is a powerful technique for characterizing solid surfaces.
• All types of inorganic solids can be analyzed.
• Elemental (except H, He) and chemical analyses within a depth of 10 nm.
• Quantitative technique.
• Extremely useful for surface treatment of materials.