Surface Analysis
The Study of the Outer-Most Layers of Materials (<100 Å).

- **Electron Spectroscopies**
  - XPS: X-ray Photoelectron Spectroscopy
  - AES: Auger Electron Spectroscopy

- **Ion Spectroscopies**
  - SIMS: Secondary Ion Mass Spectrometry

![Partially Covered Surface coverage](image)

or

![A simple thin film on a substrate](image)
X-ray Photoelectron Spectroscopy
XPS, ESCA

Photon inn – electron out

Photon self-identity problems.
Introduction to X-ray Photoelectron Spectroscopy (XPS)

- **What is XPS? - 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.
What is XPS?

X-ray Photoelectron spectroscopy, based on the photoelectric effect,\textsuperscript{1,2} was developed in the mid-1960’s by Kai Siegbahn and his research group at the University of Uppsala, Sweden.\textsuperscript{3}

\textsuperscript{1} H. Hertz, Ann. Physik 31, 983 (1887).
Introduction
X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy works by irradiating a sample material with mono energetic soft x-rays causing electrons to be ejected.

Identification of the elements in the sample can be made directly from the kinetic energies of these ejected photoelectrons.

The relative concentrations of elements can be determined from the photoelectron intensities.
XPS - ESCA

- Surface sensitive analysis technique based on photoelectric effect. Depth of analysis ~4-40 nm.
- All elements except Hydrogen.
- Wide range of materials: Polymers, Ceramics, metals …. (vacuum compatible)
- Applications: corrosion, catalysis, thin films, surface coatings, segregation …
- Gives information on chemical composition and chemical state.
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.
Auger Relation of Core Hole

- L electron falls to fill core level vacancy (step 1).
- KLL Auger electron emitted to conserve energy released in step 1.
- The kinetic energy of the emitted Auger electron is: \( KE = E(K) - E(L2) - E(L3) \).
X-ray Photoelectron Spectroscopy

Small Area Detection

Electrons can be excited in this entire volume.

X-ray excitation area ~1x1 cm². Electrons are emitted from this entire area.

Electrons are extracted only from a narrow solid angle.

X-ray beam

X-ray penetration depth ~1μm. Electrons can be excited in this entire volume.

1 mm²

10 nm
Surface Sensitivity
Surface sensitivity

Random Walk of Electron in a Lattice

This is what happens Physically

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XPS – ESCA
XPS Energy Scale- Binding energy

\[ BE = \hbar \nu - KE - \Phi_{spec} \]

Where:
- \( BE \) = Electron Binding Energy
- \( KE \) = Electron Kinetic Energy
- \( \Phi_{spec} \) = Spectrometer Work Function

Photoelectron line energies: Not Dependent on photon energy.
Auger electron line energies: Dependent on photon energy.

The binding energy scale was derived to make uniform comparisons of chemical states straightforward.
Photo emission process is often envisaged as three steps

• Absorption and ionisation - (initial state effect)

• Response from atom and creation of photoelectron - (final state effect)

• Transport of electron to surface and escape - (extrinsic loss)
Absorbing X-rays – emitting Photoelectrons

\[ E_{\text{photon}} = h\nu \]

- 700 nm, 1.77 eV: no electrons
- 550 nm, 2.25 eV: \( v_{\text{max}} = 2.96 \times 10^5 \text{ m/s} \)
- 400 nm, 3.1 eV: \( v_{\text{max}} = 6.22 \times 10^5 \text{ m/s} \)

Potassium - 2.0 eV needed to eject electron

Photoelectric effect
A closer look

\[ \text{X-ray (photon)} \]

\[ \text{1s} \]

\[ \text{2s} \]

\[ \text{2p} \]

\[ E_{\text{Fermi level}} \]

\[ \text{Binding Energy (BE)} \]

\[ \text{Photoelectron} \]
XPS Peaks

Incomplete Listing of Photoelectron Peaks
XPS example: Gold

Gold XPS wide scan spectrum

<table>
<thead>
<tr>
<th>Photoelectron Peaks</th>
<th>4s</th>
<th>4p$_{1/2}$</th>
<th>4p$_{3/2}$</th>
<th>4d$_{3/2}$</th>
<th>4d$_{5/2}$</th>
<th>5s</th>
<th>4f$_{5/2}$</th>
<th>4f$_{7/2}$</th>
<th>5f$_{1/2}$</th>
<th>5p$_{3/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energies</td>
<td>763</td>
<td>643</td>
<td>547</td>
<td>353</td>
<td>335</td>
<td>110</td>
<td>88</td>
<td>84</td>
<td>74</td>
<td>57</td>
</tr>
</tbody>
</table>

Auger Peaks

<table>
<thead>
<tr>
<th>N$<em>{67}$O$</em>{45}$O$_{45}$</th>
<th>N$<em>{5}$N$</em>{6}$N$_{57}$</th>
<th>N$<em>{4}$N$</em>{6}$N$_{57}$</th>
<th>N$<em>{5}$N$</em>{6}$V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding Energies</td>
<td>1416</td>
<td>1342</td>
<td>1324</td>
</tr>
</tbody>
</table>

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Energy resolution \( \sim 1 \text{ eV} \)

\[ 3d_{5/2} = 368.3 \text{ eV} \]
\[ \Delta = 6.00 \text{ eV} \]
Electronic structure and spectroscopy

Vacuum Level

- 2p  (BE=31eV)
- 2s  (BE=64eV)
- 1s  (BE=1072eV)

Na 1s

Mg Kα from NaCl

1072.4

Binding Energy / eV

1080 1075 1070 1065 1060 1055

Na 2p

Mg Kα from NaCl pellet etched

31.3

Binding Energy / eV

38 36 34 32 30 28 26 24 22 20
## Binding energies

### Sodium

<table>
<thead>
<tr>
<th>Label</th>
<th>Orbital</th>
<th>eV [literature reference]</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1s</td>
<td>1070.8 [3]</td>
</tr>
<tr>
<td>L_I</td>
<td>2s</td>
<td>63.5 [3]</td>
</tr>
<tr>
<td>L_{II}</td>
<td>2p_{1/2}</td>
<td>30.4 [3]</td>
</tr>
<tr>
<td>L_{III}</td>
<td>2p_{3/2}</td>
<td>30.5 [2]</td>
</tr>
</tbody>
</table>
### Chemical shift

<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>

**XPS of Poly(ethylene terephthalate)**

- Atom %
  - C = 71
  - O = 29

- % of C 1s
  - CH: 63%
  - C-O: 20%
  - O=C-O: 17%

Quantitative elemental information

Chemical state information.
Chemical shift – binding energies in C 1s peak

<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 carbon</td>
<td>C–Cl</td>
</tr>
<tr>
<td>F bound to carbon</td>
<td>C–F</td>
</tr>
<tr>
<td>carbonyl</td>
<td>C=O</td>
</tr>
<tr>
<td>amide</td>
<td>N–C=O</td>
</tr>
<tr>
<td>acid, ester</td>
<td>O–C=O</td>
</tr>
<tr>
<td>urea</td>
<td>N–C–N</td>
</tr>
<tr>
<td>carbamate</td>
<td>O–C–N</td>
</tr>
<tr>
<td>carbonate</td>
<td>O–C–O</td>
</tr>
<tr>
<td>2F bound to carbon</td>
<td>CH₂CF₂</td>
</tr>
<tr>
<td>carbon in PTFE</td>
<td>CF₂CF₂</td>
</tr>
<tr>
<td>3F bound to carbon</td>
<td>CF₃</td>
</tr>
</tbody>
</table>

*The observed binding energies will depend on the specific environment where the functional groups are located. Most ranges are ±0.2 eV, but some (e.g., fluorocarbon samples) can be larger.
Spin-Orbit Coupling

Orbital = \( p \)

\( l = 1 \)

\( s = \pm \frac{1}{2} \)

\( l s = \frac{1}{2}, \frac{3}{2} \)
Spin-orbital splitting

Peak Notations
L-S Coupling ($j = l \pm s$)

$\ell = 0...s$
1...p
2...d
3...f

$n$

$2p_{3/2}$

$j = \ell - s$
$j = \ell + s$

<table>
<thead>
<tr>
<th>$l$</th>
<th>$p$</th>
<th>$d$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$p_{1/2}$</td>
<td>$d_{3/2}$</td>
<td>$f_{5/2}$</td>
</tr>
<tr>
<td>2</td>
<td>$p_{3/2}$</td>
<td>$d_{5/2}$</td>
<td>$f_{7/2}$</td>
</tr>
</tbody>
</table>

$s = -1/2$
$s = +1/2$

Area ratio: $1 : 2$
Area ratio: $2 : 3$
Area ratio: $3 : 4$
Instrumentation

Surface analysis by XPS requires irradiating a solid in an Ultra-high Vacuum (UHV) chamber with monoenergetic soft X-rays and analysing the energies of the emitted electrons.
XPS instrument at UIO?

Kratos Axis Ultra – new in 2007
People at UiO/Sintef

Martin

Spyros
Instrument

1. Chambers
2. Vacuum and Pumps
3. Sources
4. Monochromator
5. Analysers

Specimen handling
Planning experiments
Dual anode X-ray source

Fig. 3. Double-anode X-ray source.

The two components of the $K_\alpha$ spectrum ($K_{\alpha_1} + K_{\alpha_2}$) which comprise the $K_\alpha$ spectrum of Al. [Spectrum from Siegbahn et al., 1967.]
Alternative X-ray sources

**TABLE 1**
Some X-ray lines of use in photoelectron spectroscopy

<table>
<thead>
<tr>
<th>Line</th>
<th>Be K</th>
<th>Y M_ξ</th>
<th>Zr M_ξ</th>
<th>Nb M_ξ</th>
<th>Mo M_ξ</th>
<th>Ru M_ξ</th>
<th>Rh M_ξ</th>
<th>C K</th>
<th>Ti Li</th>
<th>Ti La</th>
<th>O K</th>
<th>Cr La</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (eV)</td>
<td>108.9</td>
<td>132.3</td>
<td>151.4</td>
<td>171.4</td>
<td>192.3</td>
<td>236.9</td>
<td>260.1</td>
<td>278</td>
<td>395.3</td>
<td>452.2</td>
<td>524.9</td>
<td>572.8</td>
</tr>
<tr>
<td>Width (eV)</td>
<td>5.0</td>
<td>0.47</td>
<td>0.77</td>
<td>1.21</td>
<td>1.53</td>
<td>2.49</td>
<td>4.0</td>
<td>6</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Line</td>
<td>Ne Ka</td>
<td>Ni La</td>
<td>Cu La</td>
<td>Zn La</td>
<td>Na Ka</td>
<td>Mg Ka</td>
<td>Al Ka</td>
<td>Zr La</td>
<td>Ti K</td>
<td>Cr Ka</td>
<td>Cu Ka</td>
<td></td>
</tr>
<tr>
<td>Energy (eV)</td>
<td>849</td>
<td>851.5</td>
<td>929.7</td>
<td>1011.7</td>
<td>1041.0</td>
<td>1253.6</td>
<td>1486.6</td>
<td>2042</td>
<td>4510</td>
<td>5417</td>
<td>8048</td>
<td></td>
</tr>
<tr>
<td>Width (eV)</td>
<td>0.3</td>
<td>2.5</td>
<td>3.8</td>
<td>2.0</td>
<td>0.42</td>
<td>0.7</td>
<td>0.85</td>
<td>1.7</td>
<td>2.0</td>
<td>2.1</td>
<td>2.6</td>
<td></td>
</tr>
</tbody>
</table>