X-Ray Photoelectron Spectroscopy (XPS)

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Electron Spectroscopy for Chemical Analysis (ESCA)
The basic principle of the photoelectric effect was enunciated by Einstein [1] in 1905:

\[ E = h\nu \]

There is a threshold in frequency below which light, regardless of intensity, fails to eject electrons from a metallic surface. \( h\nu_c > e\Phi_m \) where \( h \) is the Planck constant (6.62 \times 10^{-34} \text{ J s}) and \( \nu \) the frequency of the radiation.

In photoelectron spectroscopy such XPS, Auger and UPS, the photon energies range from 20 -1500 eV (even higher in the case of Auger, up to 10,000 eV) much greater than any typical work function values (2-5 eV).

In these techniques, the kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted electrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyzer and a photoelectron spectrum can thus be recorded.

• By using photo-ionization and energy-dispersive analysis of the emitted photoelectrons the composition and electronic state of the surface region of a sample can be studied.

• Traditionally, these techniques have been subdivided according to the source of exciting radiation into:
  • **X-ray Photoelectron Spectroscopy (XPS or ESCA)** - using soft x-ray (200 - 1500 eV) radiation to examine core-levels.
  • **Ultraviolet Photoelectron Spectroscopy (UPS)** - using vacuum UV (10 - 45 eV) radiation to examine valence levels.
  • **Auger Electron Spectroscopy (AES or SAM)** – using energetic electron (1000 – 10,000 eV) to examine core-levels.

• Synchrotron radiation sources have enabled high resolution studies to be carried out with radiation spanning a much wider and more complete energy range (5 - 5000+ eV) but such work will remain, a very small minority of all photoelectron studies due to the expense, complexity and limited availability of such sources.
One way to look at the overall photoelectron process is as follows:

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

1. Conservation of energy then requires that:
\[ E(A) + h\nu = E(A^+) + E(e^-) \quad \text{(energy is conserved)} \]

2. Since the energy of the electron is present solely as kinetic energy (KE) this can be rearranged to give the following expression for the KE of the photoelectron:
\[ E(e^-) = KE(e^-) = h\nu - [E(A^+) - E(A)] \]

3. The final term in brackets represents the difference in energy between the ionized and neutral atoms, and is generally called the binding energy (BE) of the electron - this then leads to the following commonly quoted equation:
\[ KE = h\nu - BE \]
Photoelectrons: \( BE = h\nu - KE - \Phi_s \)
Energy Diagram

- $E_b$ (binding energy) is below the conduction band edge.
- Fermi energies of the metal and the spectrometer line-up (electrons transfer between metal and spectrometer until the $E_F$ are aligned).
- Contact potential is $e(\phi - \phi_{sp})$.
- $E'_k$ is the energy measured.
- $E_b = h\nu - E'_k - e\phi_{sp}$ (no need to know the work function of the sample)
X-ray Sources

• Their choice is determined by the energy resolution. Typical materials are Mg, Al and Ag.
• A heated filament (cathode) emits electrons which are accelerated toward a solid anode (water cooled) over a potential of the order of 5 -20 kV.
• Holes are formed in the inner levels of the anode atoms by the electron bombardment and are then radioactively filled by transitions from higher-lying levels:

\[
\begin{align*}
2p_{\frac{3}{2}} & \rightarrow 1s \\
2p_{\frac{1}{2}} & \rightarrow 1s
\end{align*}
\]

Resulting in the emission of X-rays

- Mg Kα₁,₂ at 1253.6 eV
- Al Kα₁,₂ at 1486.6 eV
Typical geometry of an x-ray gun

Incident beam
\[ E = h\nu \]

Escaped Si K\(_{\alpha}\) X-ray
\(~1.74\) keV

Aluminum windows of 10-30 \(\mu\)m thick separate the excitation region from the specimen.

Additional x-ray lines (\(K\alpha_3\) and \(K\alpha_4\)) and a continuous spectrum (Bremsstrahlung) are produced. Peaks 10 eV above the \(K\alpha_{1,2}\) with intensities of 8 % and 4 % of \(K\alpha_{1,2}\) and a continuous spectrum contribute to the BG.
### Available x-ray Sources

<table>
<thead>
<tr>
<th>X-rays</th>
<th>Energy (eV)</th>
<th>Natural Width (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu K(\alpha)</td>
<td>8048</td>
<td>2.5</td>
</tr>
<tr>
<td>Ti K(\alpha)</td>
<td>4511</td>
<td>1.4</td>
</tr>
<tr>
<td>Ag L(\alpha)</td>
<td>2984</td>
<td>2.6</td>
</tr>
<tr>
<td>Al K(\alpha)</td>
<td>1487</td>
<td>0.9</td>
</tr>
<tr>
<td>Mg K(\alpha)</td>
<td>1254</td>
<td>0.8</td>
</tr>
<tr>
<td>Na K(\alpha)</td>
<td>1041</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Kratos and PHI commonly use AlK\(\alpha\) and MgK\(\alpha\)
• To remove the unwanted radiation and increase the energy resolution the AlKα is often monochromatized (cut a “slice” from the x-ray energy spectrum, removing both satellites and Bremstrahlung (which increases the BG level).

• *Crystal used* = quartz because can be obtained in near perfect form and can be elastically bent (bending does not affect resolution or reflectivity).

\[
\lambda = 2d \sin(\theta)
\]

For first order diffraction \((n = 1)\) and for AlKα x-rays, \(\lambda = 8.3 \text{ Å} \) and the Bragg angle, \(\theta\) is 78.5°
Rowland circle

The crystal must lie along the circumference of the Rowland circle (focusing circle), Johann focusing geometry.
Dispersive analysis of the kinetic energy spectrum $n(KE)$

A field is applied between 2 parallel plates, distance $s$ apart. The lower plate has slits a distance $r$ apart (entrance and exit slits). The photoelectrons with kinetic energy $KE$ are transmitted to the detector. By varying $V_d$ the spectrum of electron kinetic energies can thus be obtained. $KE$ is proportional to $V_d$ therefore the plot of electron flux at the detector against $V$ is the photoemission spectrum.

$$V_d = \frac{2sKE}{er}$$
The alternative to dispersive analysis is to discriminate the electron KE by a retarding electric field applied between the target region and the detector. Electrons with KE > eV_r will reach the detector (a kind of filtration process).
Photoionization process has a rather low absolute probability ($10^4$ electrons per second, or $10^{-15}$ A) therefore electron multipliers, CEM (gain of $10^6$) are used to obtain an accurately measurable current. Newer instruments use channel plates.

**Components:**
1. Source of radiation
2. Ionization Chamber
3. Electron energy analyzer
4. Electron detector
5. High vacuum system software and computer

Figure 5. AXIS 165 Spectrometer Schematic
Immediate identification of the chemical composition of the surface (≤ 1% atomic percent).

The core electron binding energies (BE) of the elements are distinctive
*High-resolution* acquisition scans yield information such as:

- *Chemical shifts* (covalent or ionic bonds)
- *Multiplet structure*
- *Satellites*
- *Chemical bonding*
Surface Sensitive Technique

- XPS is very surface sensitive because only electrons from the top few atomic layers (mean free path ~1.5 nm) can escape without loss of energy.

- The absorption length of the X-rays is about 100 nm to 1000 nm.
AXIS-165 multi-electron spectrometer

From Kratos analytical Inc.
A sample placed in ultra-high vacuum is irradiated with photons of energy $(h\nu)$; soft x-rays. Atoms on the surface emit electrons (photoelectrons) after direct transfer of energy from the photons to the core-level electron.

**Summary**

1. A bound electron absorbs the photon, converting some of its energy into kinetic energy.

2. As the electron leaves the atom some of its energy is used to overcome the Coulomb attraction of the nucleus, reducing its KE by its initial state BE.

3. At the same time the outer orbitals readjust, lowering the energy of the final state that is being created and giving this additional energy to the outgoing electron.
References


• Practical Surface Analysis by D. Briggs and M. P. Seah.

Websites:

http://srdata.nist.gov/xps,
http://www.xpsdata.com,
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