X-Ray Photoelectron Spectroscopy (XPS)

Auger Electron Spectroscopy (AES)
XPS

- X-ray photoelectron spectroscopy (XPS) is one of the most used techniques to chemically characterize the surface. Also known as electron spectroscopy for chemical analysis (ESCA).

- It allows qualitative and quantitative **elemental analysis** from the surface to a depth of the order of a few nanometers.
Radiation - matter interaction
Photoelectric effect

X-ray absorption is very fast ~$10^{-16}$ s

From picture,
- no photoemission from levels with $h\nu < BE + \phi$
- KE of photoelectron increases as BE decreases
- intensity of photoemission $\propto$ intensity of photons
- need monochromatic (X-ray) radiation
- a range of KE's can be produced if valence band is broad
- since each element has unique set of core levels, KE's can be used to fingerprint element

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

Ejected electrons with
\[ E_k = h\nu - E_b - \phi \]

Normal to the surface

\[ \text{Sample} \]

\[ \text{X-ray} \]

Since the work function, \( \Phi \), can be compensated artificially, it is eliminated, giving the binding energy as follows:

\[ \text{BE} = h\nu - \text{KE} \]

\( h\nu \) - X-ray photon energy
(for Al K\( \alpha \), \( h\nu = 1486.6 \text{ eV} \))

\( \text{KE} \) - kinetic energy of photoelectron, which can be measured by the energy analyzer

\( \Phi \) - work function induced by the analyzer, about 4~5 eV.
XPS spectra (wide scan)

The maximum possible energy depends on the wavelength used (Al Kα – 1486.6 eV; Mg Kα – 1253.6 eV)
When a sample looses electrons, or an atom is bonded to more electronegative atoms, the electrons have less screening effect and require more energy to be extracted, this is the cause for chemical shifts.
High energy incident photons on a surface create characteristic electrons relatively deep in the solid.

Only those electrons created near the surface escape without loss of energy:
Attenuation length

- **Attenuation length** is defined as the distance at which the probability of electron escape from a solid, without the occurrence of inelastic scattering, drops of 1/e (i.e. 1/2.71 or 36.8%).

- The term **escape depth** is defined for the electrons travelling normal to the surface and is given by the attenuation length times the cosine of the angle between the direction of electron travel and the normal to the surface.
Electrons have maximum interaction with solids for ~50 eV. At higher and lower energies, this interaction decreases and the attenuation length goes up. Maximum sensitivity occurs for ~5-20 Å.
XPS spectra (wide scan)
Background shape

XPS spectra show characteristic "stepped" background (intensity of background at higher BE of photoemission peak is always greater)

Due to inelastic processes (extrinsic losses) from the bulk:

- Only electrons close to surface can, on average, escape without energy loss
- Electrons deeper in surface loose energy and emerge with reduced KE and increased BE
- Electrons very deep in surface loose all energy and cannot escape

\[ BE = h\nu - KE \]
Background shape

Energy losses

Mean photoelectron binding energy

Background

Intensity (photoelectrons per second)

XPS spectrum

1000

BE (eV)

0

2s

2p

3s

3d
# Qualitative analysis

<table>
<thead>
<tr>
<th>Photoelectric Peaks</th>
<th>Due to photoelectrons created within the first few atomic layers (elastically scattered).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical shifts</td>
<td>Positive (higher BE): atom gives electrons&lt;br&gt;Negative (lower BE): atom receives electrons</td>
</tr>
<tr>
<td>Doublet</td>
<td>Result of spin-orbit interaction.</td>
</tr>
<tr>
<td>Multiplet</td>
<td>Can occur when the system has unpaired electrons in the valence levels.</td>
</tr>
<tr>
<td>Auger peaks</td>
<td>Auger electron is initiated by the creation of an ion with an inner shell vacancy. Auger electrons are emitted in the relaxation of the excited ion.</td>
</tr>
<tr>
<td>Valence band</td>
<td>Photoelectrons from molecular orbitals. The analysis of these bands is useful in studying the electronic structure of materials.</td>
</tr>
<tr>
<td>Satellite Peaks</td>
<td>Arise when a core electron is removed by a photoionization. There is a sudden change in the effective charge due to the loss of shielding electrons. (This perturbation induces a transition in which an electron from a bonding orbital can be transferred to an anti-bonding orbital simultaneously with core ionization).</td>
</tr>
<tr>
<td>Energy losses</td>
<td>Occur at higher binding energies (lower kinetic energies).</td>
</tr>
<tr>
<td>Plasmon Peaks</td>
<td>Are created by collective excitations of the valence band.</td>
</tr>
</tbody>
</table>
Charge and chemical shifts

- **Charge shifts:** Samples should be conductive, since they become positive when loosing electrons and a positive voltage retards the electrons reaching the sample – this causes a charge shift.

- **Chemical shifts:** change in binding energy of a core electron of an element due to a change in the chemical bonding of that element
Charge and chemical shifts

How to distinguish between chemical and charge shifts?
- Charge shifts affect all peaks the same way, while chemical shifts affect only specific peaks and sometimes in an opposite way.

How to compensate for the charge shifts?
- By adjusting the voltage or by using a flood gun, that gives electrons compensating the positive effect on the sample.
Chemical Information

Elements present at the surface

XPS spectrum of a BaO surface
XPS of Copper-Nickel alloy

Chemical Information

Elements present at the surface and their concentration

<table>
<thead>
<tr>
<th></th>
<th>Peak Area</th>
<th>Rel. Sens.</th>
<th>Atomic Conc %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>2.65</td>
<td>4.044</td>
<td>49</td>
</tr>
<tr>
<td>Cu</td>
<td>3.65</td>
<td>5.321</td>
<td>51</td>
</tr>
</tbody>
</table>

- **Cu 2p**
- **Ni 2p**
- **Cu LMM**
- **Ni LMM**
- **Ni 3p**
- **Cu 3p**
XPS RESULT

Chemical Information – XPS is sensitive to the oxidation state
Oxidation states of the elements present at the surface

SiO\textsubscript{2}

Si 2p ionization spectrum (detail)

Metallic Si

Presence of SiO\textsubscript{2}
XPS analysis showed that the pigment used on the mummy wrapping was Pb$_3$O$_4$ rather than Fe$_2$O$_3$.
Auger Spectroscopy
Auger spectroscopy

- Auger electron emission - basis of Auger electron spectroscopy (AES)
- X-ray fluorescence
Auger electrons

Relative Probabilities of Relaxation of a K Shell Core Hole

Note: The light elements have a low cross section for X-ray emission.
Auger electrons
SPACIAL RESOLUTION

Auger Resolution < 10 nm

Depends:
Diameter of incident beam
Energy of incident beam
EXAMPLE - Auger spectrum of Silicon

1 – Exit of level K electron (Eb=1844 eV)
2 – Decay of a L\text{2,3} level electron (Eb=104 eV)
(Excess of energy: 1844 – 104 = 1740 eV)
3 – Release of a L\text{2,3} level electron (Eb = 104 eV)
(Auger KL\text{2,3}L\text{2,3} electron with KE = 1636 eV)
AUGER RESULT
XPS RESULT

XPS spectrum of a BaO surface
Instrumentation

XSAM800 KRATOS spectrometer
Instrumentation

Introduction chamber (XSAM800 KRATOS spectrometer)
The analyzer is regulated for a certain energy range by a retarding field. Only the electrons in that range can curve along the detector, higher energy electrons go straight ahead, while lower energy electrons curve too fast.
DETAIL OF ANALYSER

- Electron source
  “Field emission type”
- Electron gun
- Ion gun
- Analysor
- Lens
- Detector
- Sample

Vacuum ~\(10^{-9}\) mbar
Sample Zone

Electron beam

Ion gun

analyser

Different tilt angles

Sample holder

Sample
ASSOCIATED TECHNIQUES

SEM

Electron guns

Analyzer

Ion gun - Canhão de iões

Electron backscattered detector – Detector de electrões retrodifundidos

Photon source (XPS)
Instrumentation

- X-ray source:
  - Mg Kα radiation: \( h\nu = 1253.6 \text{ eV} \)
  - Al Kα radiation: \( h\nu = 1486.6 \text{ eV} \)
- Ion Gun
- Hemispherical sector analyzer and electrostatic lenses
- Vacuum: better than \( 10^{-8} \text{ Pa} \)
- Detection system (XPS, Auger, SEM)
Why UHV for Surface Analysis?

- 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.

Degree of Vacuum

<table>
<thead>
<tr>
<th>Low Vacuum</th>
<th>Medium Vacuum</th>
<th>High Vacuum</th>
<th>Ultra-High Vacuum</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^2</td>
<td>10^-1</td>
<td>10^-4</td>
<td>10^-8</td>
</tr>
</tbody>
</table>

Pressure Torr
Quantitative analysis

Quantitative analysis is based on the area of peaks and depends on the correct baseline and the sensitivity factors.

An atom might need 5-10 eV to ionize one electron, while other atom might require 100 eV to ionize it. So each element has a specific sensitivity factor.

The limit of detection is ~0.1%, but it depends on:
- Sensitivity factor
- Number of scans - wide scan or short scan (100 to 500 scans if necessary)
- So it depends on the expected results.

H and He cannot be analyzed, since they don’t have core electrons and have no characteristic energy to allow for precise identification.

The presence of two anodes in the equipment allows for peak differenciating between XPS and Auger peaks. Auger peaks shift by the difference between the 2 anodes (Al and Mg, for example).
APPLICATION EXAMPLES
AES / XPS
SURFACE ANALYSIS TECHNIQUE

- Analyse the first few atomic layers
- Qualitative and quantitative chemical information
- In-depth information
- Spatial distribution

APPLICATIONS
- Semiconductors
- Chemistry and pharmaceutical industry
- Polymers
- Materials and biomaterials
- Metallurgy
- Biochemistry, …
AUGER INFORMATION

• CHEMICAL INFORMATION
  - Elements present on the surface

• ELEMENTAL QUANTIFICATION
  - Relative atomic percentage of each element

• INFORMATION ON THE CHEMICAL STATE
  - Oxidation states of the elements

• IN-DEPTH DISTRIBUTION
  - Auger profile: in-depth concentration and layer thicknesses

• AUGER MAPS
  - Spatial distribution of the elements on the surface
Elements detected: Ni, Cu, S, Cl, C, Ca, N, O.

Detection Limit: 0.1 – 1%
IN-DEPTH DISTRIBUTION

Auger Profile

Aço 316 L
After mechanical polishing

Aço 316 L
Passivated
SPATIAL DISTRIBUTION

Auger Maps (Scanning Auger Microprobe - SAM)

SEM image of a steel superface (10 kX)

Auger electron map of Fe, Sb and Cr
Chemical changes of a Pd catalyst during its lifetime.

Diagram showing changes in Pd 3d, PdO, and PdO2 with different stages of catalyst usage: Recente, Usado, Muito usado, and Deteriorado.
DEGRADAÇÃO DE TINTAS

Tinta: PVDF + PMMA
efeito da temperatura
Silicon contamination in the head of a Carbon disk
Identification of deposited layers over an Al disk used in computers

4 layers can be identified: C, Co, Cr e Ni
Summary of Surface Techniques

- AES and XPS
- RBS
- PIXE
- SIMS

XPS: X-ray Photoelectron Spectroscopy
AES: Auger Electron Spectroscopy
RBS: Rutherford Backscattering
SNMS: Plasma-based Sputtered Neutral Mass Spectrometry
SIMS: Secondary Ion Mass Spectrometry
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