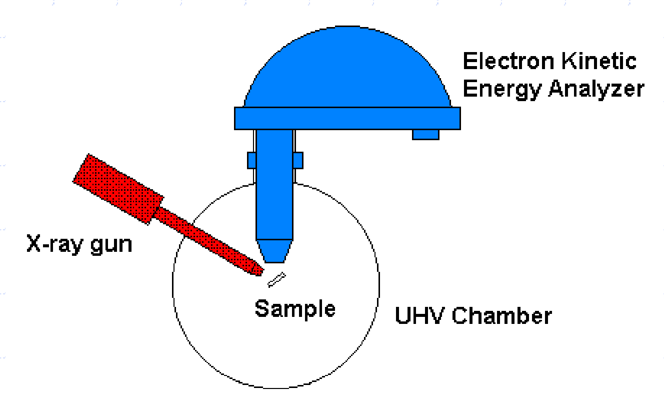
Spectroscopic Analytical Techniques

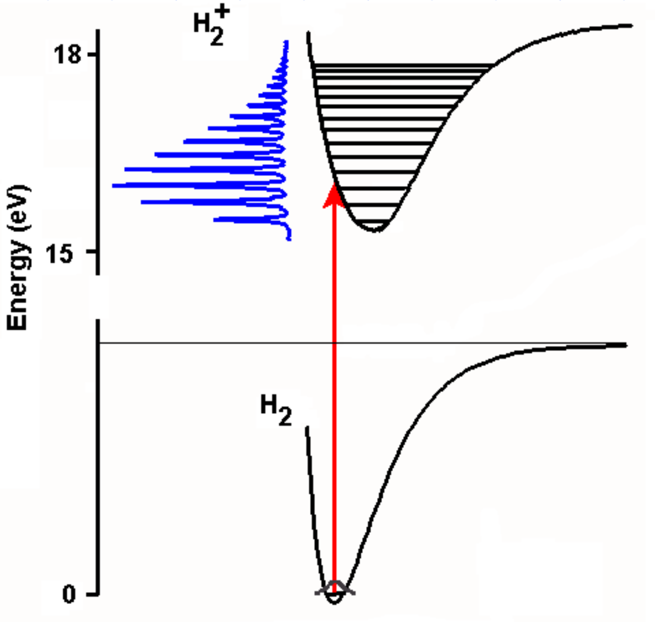
Auger Electron Spectroscopy

X-Ray Photoelectron Spectroscopy

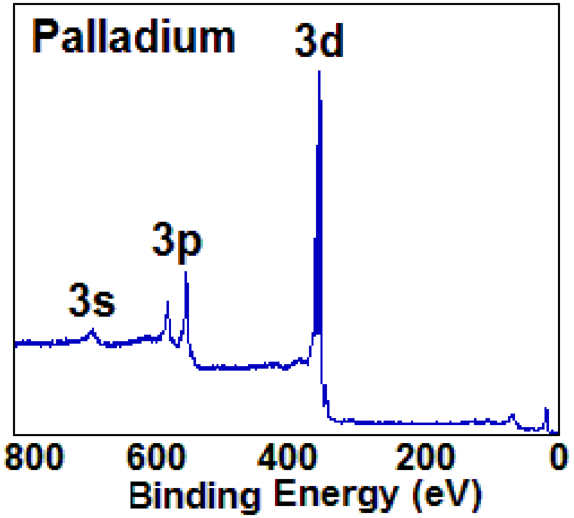
Nuclear Magnetic Resonance

Photoelectron detection

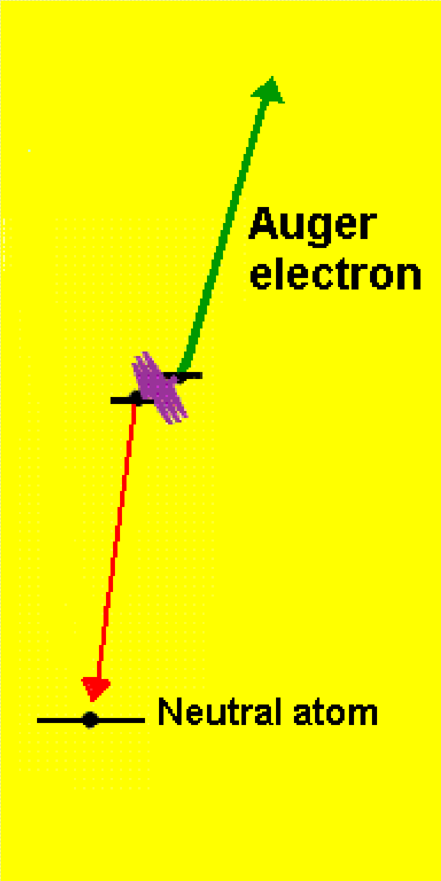




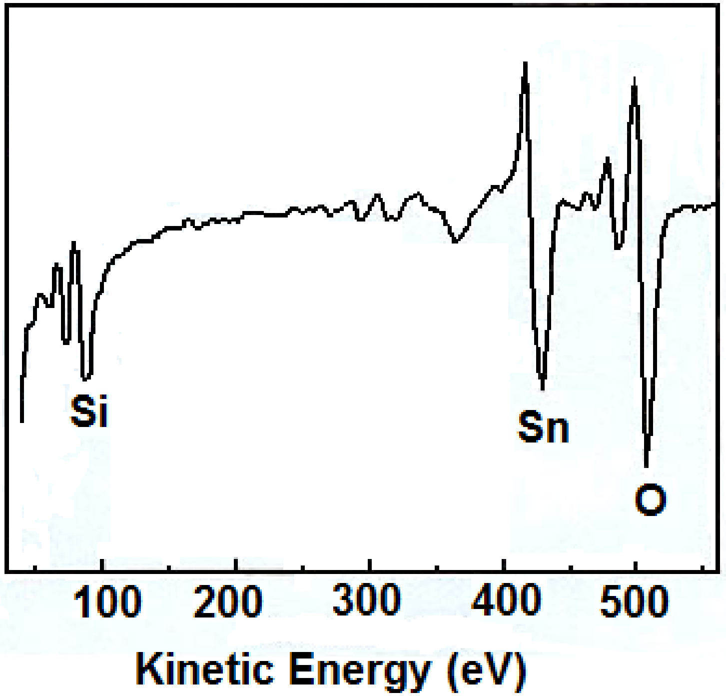
- Source of X-radiation
- Electron's kinetic energy determination
- Must be in high vacuum
- Determines the electronic state energies of the ion



Auger electrons



- Ejection of core electrons leaves the ion in an excited state
- Relaxation may produce ejection of further electrons with excess kinetic energy
- Can measure the Auger electron energies to determine information on the atom



Pronunciation and History

The **Auger effect** (pronounced */AW-zhər*) is a phenomenon in physics in which the transition of an electron in an atom filling in an inner-shell vacancy causes the emission of another electron. When an electron is removed from a core level of an atom, leaving a vacancy, an electron from a higher energy level may fall into the vacancy, resulting in a release of energy. Although sometimes this energy is released in the form of an emitted photon, the energy can also be transferred to another electron, which is ejected from the atom. This second ejected electron is called an **Auger electron**.

The name "Auger effect" comes from one of its discoverers, Pierre Victor Auger, and not from the similarly-named device, the auger.

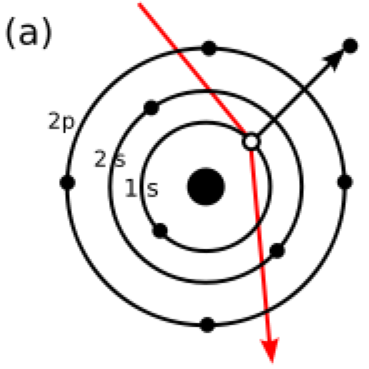
Pronunciation and History

Auger Electron Spectroscopy (AES), is a widely used technique to investigate the composition of surfaces.

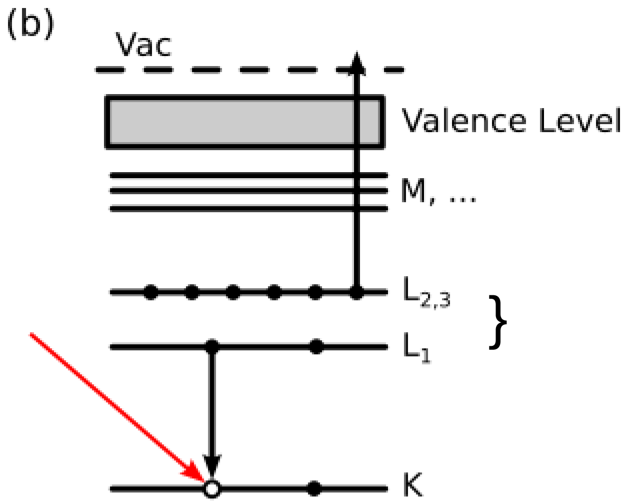
First discovered in 1923 by Lise Meitner and later independently discovered once again in 1925 by Pierre Auger [1]

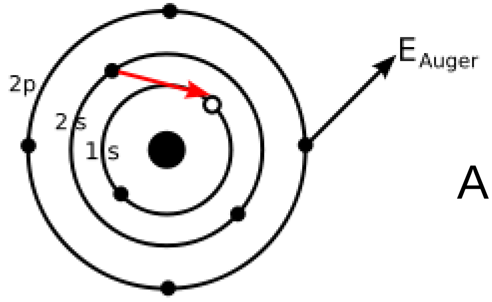
1. P. Auger, *J. Phys. Radium*, **6**, 205 (1925).

Schematically:



Electron collision





Auger electron emission

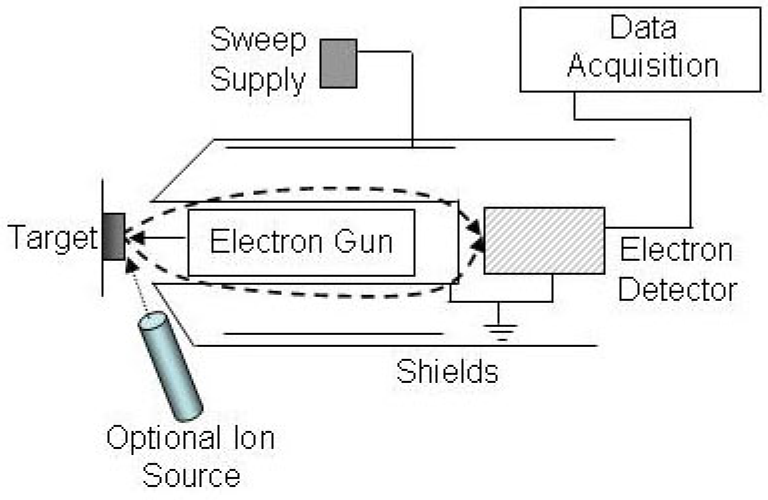
An emitted electron will have a kinetic energy of:

$$E_{kin} = E_{\text{Core State}} - EB - EC'$$

Or for the diagram above:

$$E_{kin} = K - L_1 - L_{2,3}$$

Instrumentation:



Electron energy used: 50 ev-3kV;
Escape Depth: a few nanometers
Surface sensitive technique

Little math:

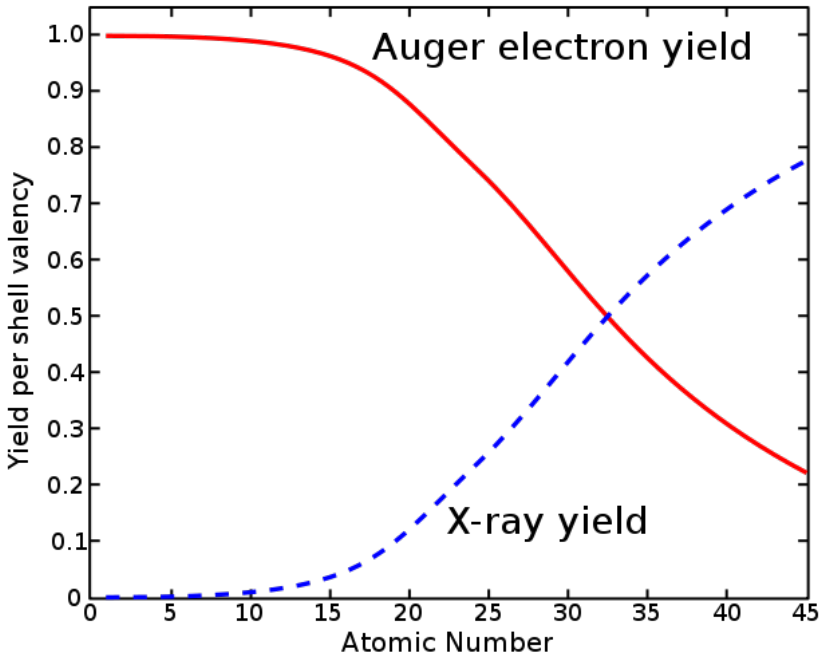
Since the intensity of the Auger peaks may be small compared to the noise level of the background, AES is often run in a derivative mode to highlight the peaks by modulating the electron collection current via a small applied AC voltage. Since this $\Delta V = k\sin(\omega t)$, the collection current becomes $I(V + k\sin(\omega t))$.
Taylor expansion gives:

$$I(V + k\sin(\omega t)) \approx I_0 + I'(V + k\sin(\omega t)) + O(I'')$$

Thus, detecting the signal at frequency ω will give a value for I' or $\frac{dN}{dE}$

Caution: the peak in derivative mode is not the true Auger peak, but rather the point of maximum slope of $N(E)$, but this is normally ignored

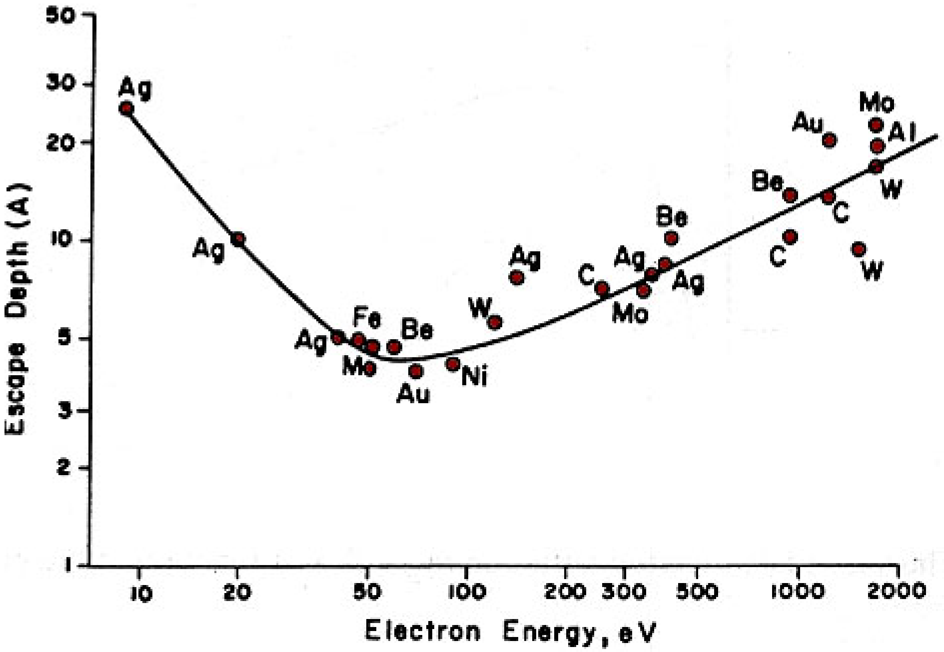
Quantitative Analysis in AES



Remember that the Auger process is not the only way for the atoms to relax; alternatively, they may undergo a radiative relaxation emitting fluorescence photons.

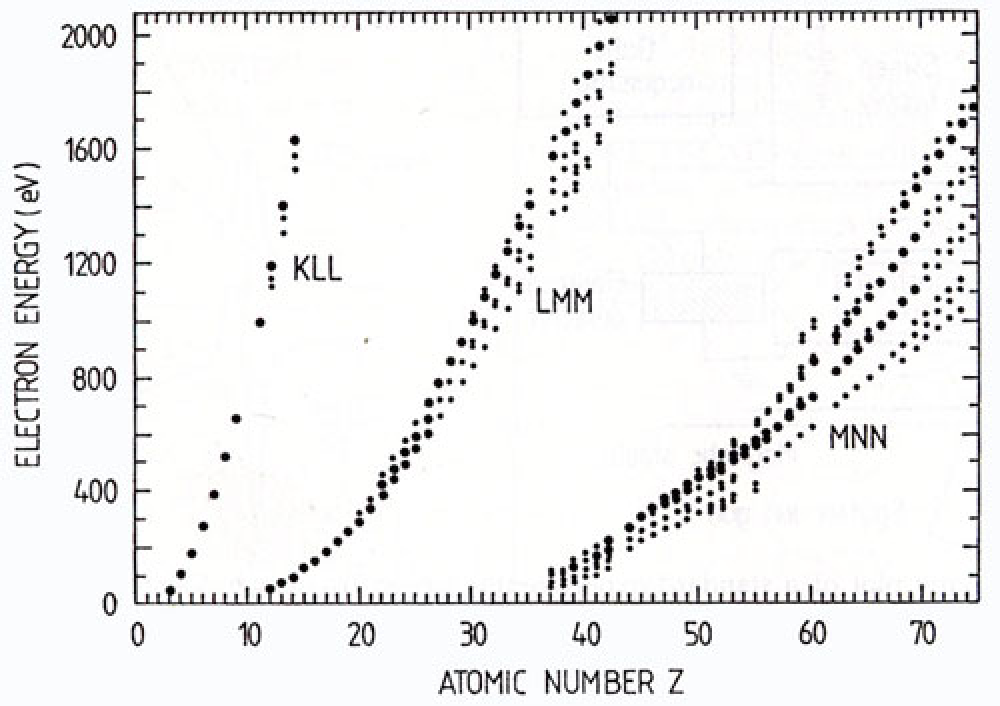
Lighter elements are more likely to undergo the Auger process (although you can not detect anything lighter than Li in the gas phase since it is a three-electron process).

Electron escape depth in metals



John B. Hudson. *Surface Science*

Elements and Energies



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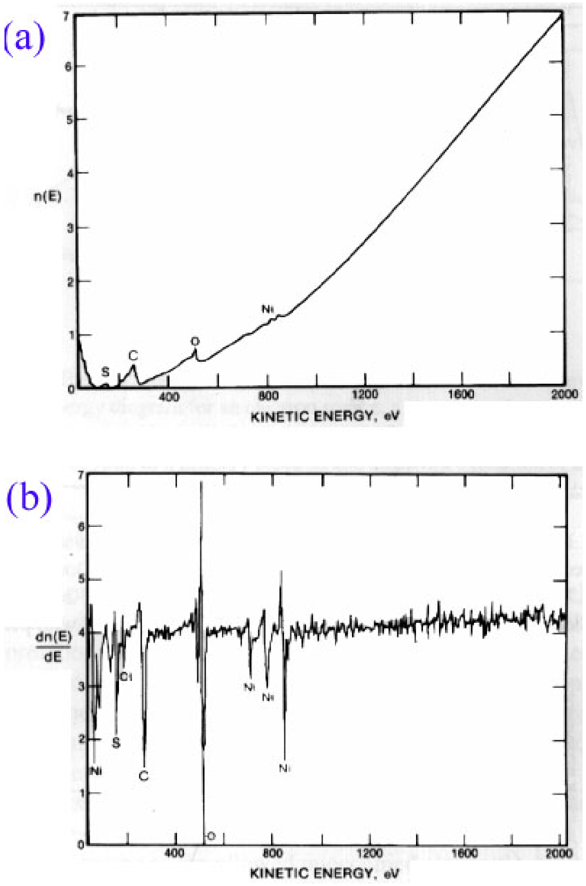
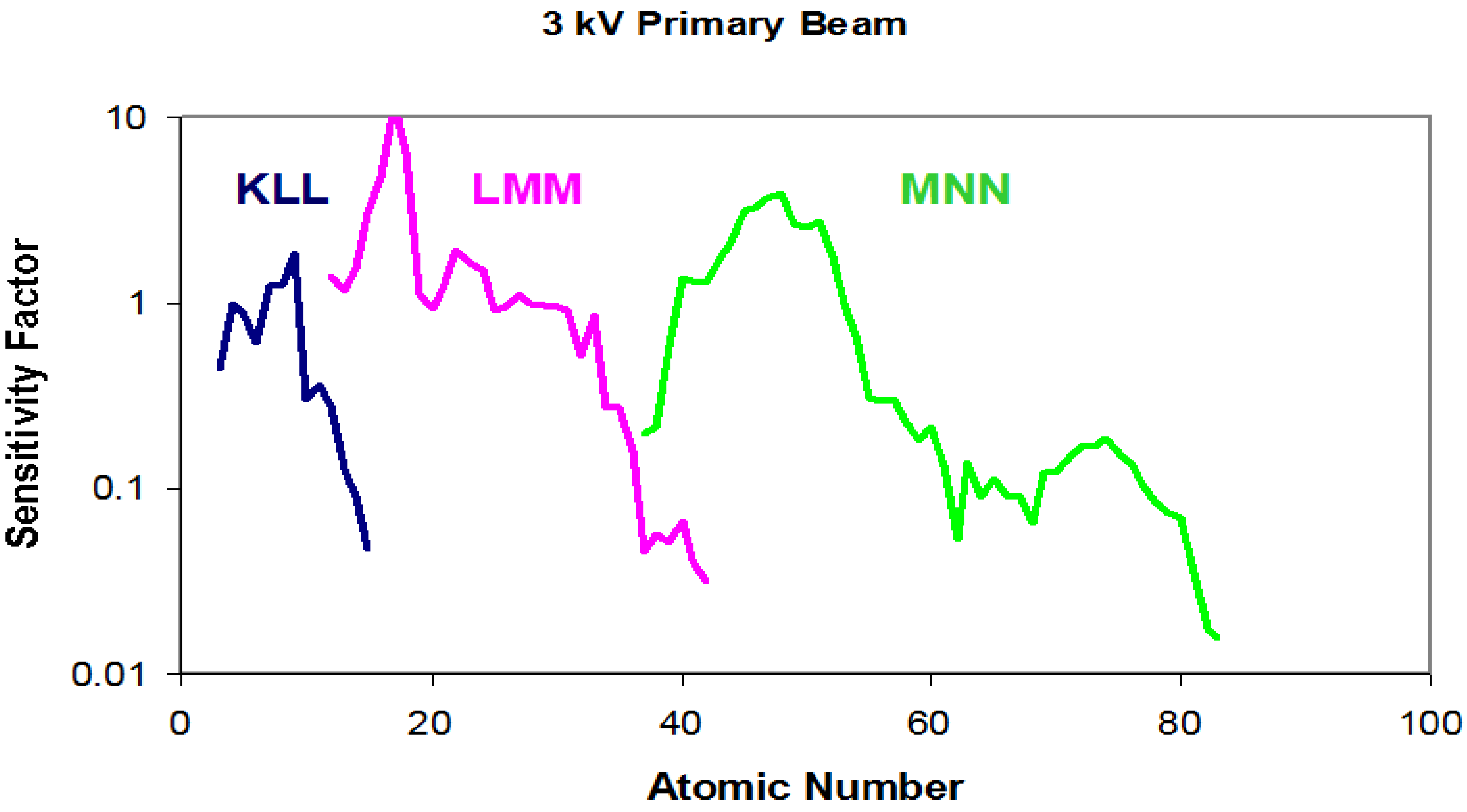
Spectra:



The Auger spectrum from a contaminated nickel surface is shown. Part (a) shows the number of electrons versus electron kinetic energy. Part (b) is the derivative of the curve in part (a). [From John B. Hudson. Surface Science. [Stoneham, MA: Butterworth-Heinemann (1992) ISBN 0 7506 9159-X]. Figure 2 was originally in C. B. Drake. J. Vac. Sci. Techn. 13, 761 (1976).p]

Spectra:



Concentations obtained based on peak intensities should be corrected for the sensitivity factors based on a specific electron transition for a specific elements (See Handbook of Auger Electron Spectroscopy, C.L Hedberg (Published by Physical Electronics, Inc.))

To do it:

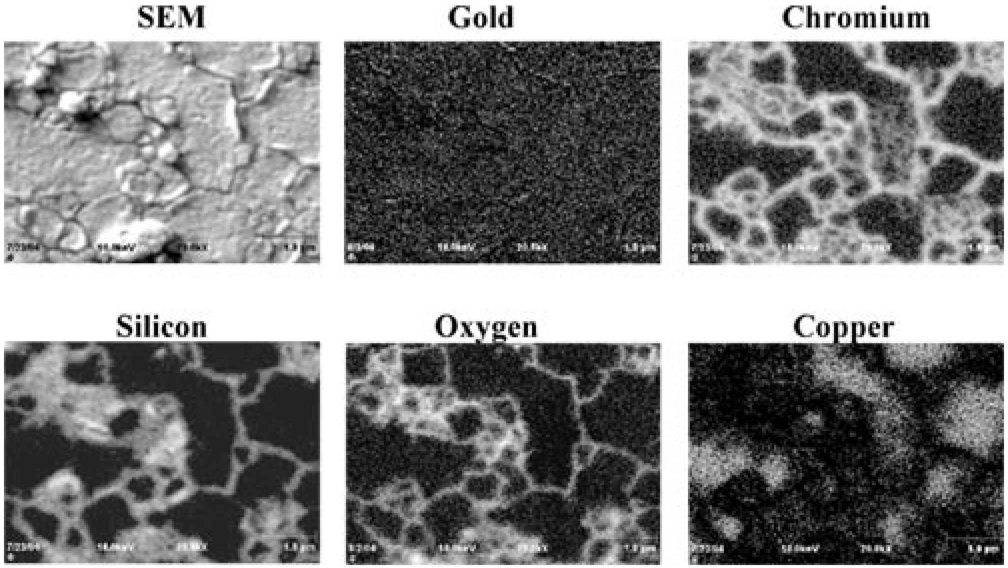
Determine the mole fraction of component A in a binary mixture of A and B:

$$x_A = \frac{I_A / s_A}{I_A / s_A + I_B / s_B}$$

Here, I is the intensity of the peak corresponding to a component and s is a relative sensitivity factor (from the handbook)

Spacially Resolved AES

Exceptional resolution, about 100 nm
High scanning rate
Map out the elements in a sample of the size of microns



Advantages and Limitations

Extremely reliable and reproducible

Standard surface analysis technique

Instant surface concentration of the elements

Great spacial resolution

Can even do depth profiling with light ion sputtering

Needs UHV

Only surface sensitive

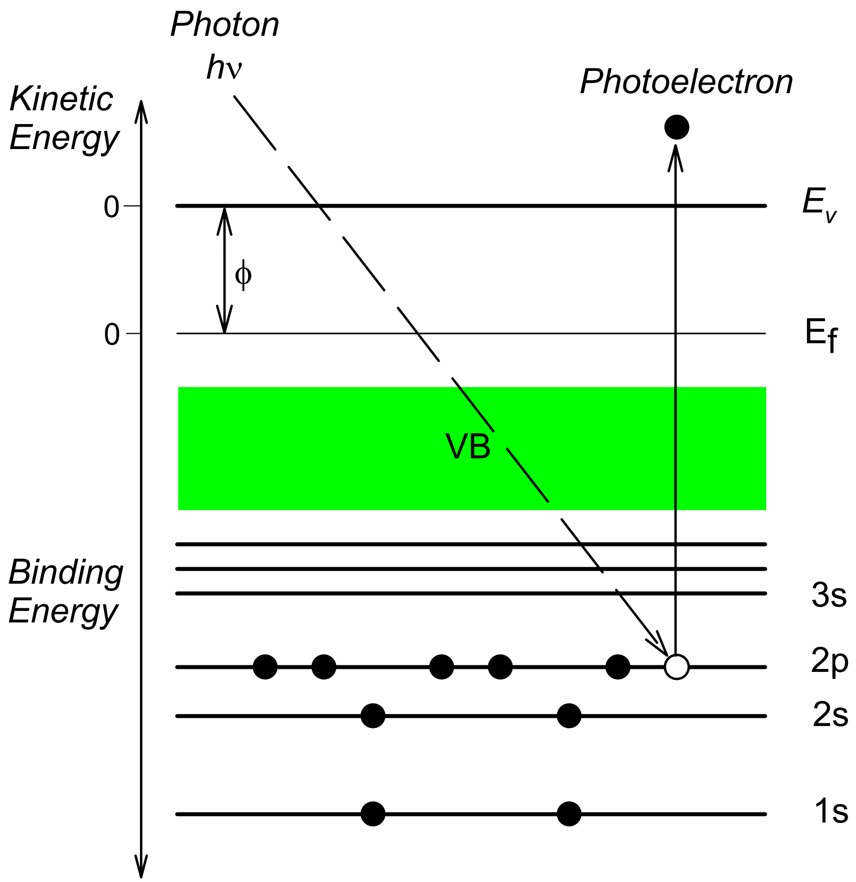
Needs careful calibration

Intensity may be obscured by secondary phenomena and may depend on a chemical state of the element

Somewhat difficult to calibrate for adsorbates on surfaces or for layered structures

Analytical Methods

--- X-ray Photoelectron Spectroscopy (XPS)



$$KE = h\nu - (E_B + \varphi)$$

XPS spectrum:
Intensities of photoelectrons versus E_B or KE

- — Elemental identification and chemical state of element
- — Relative composition of the constituents in the surface region
- — Valence band structure

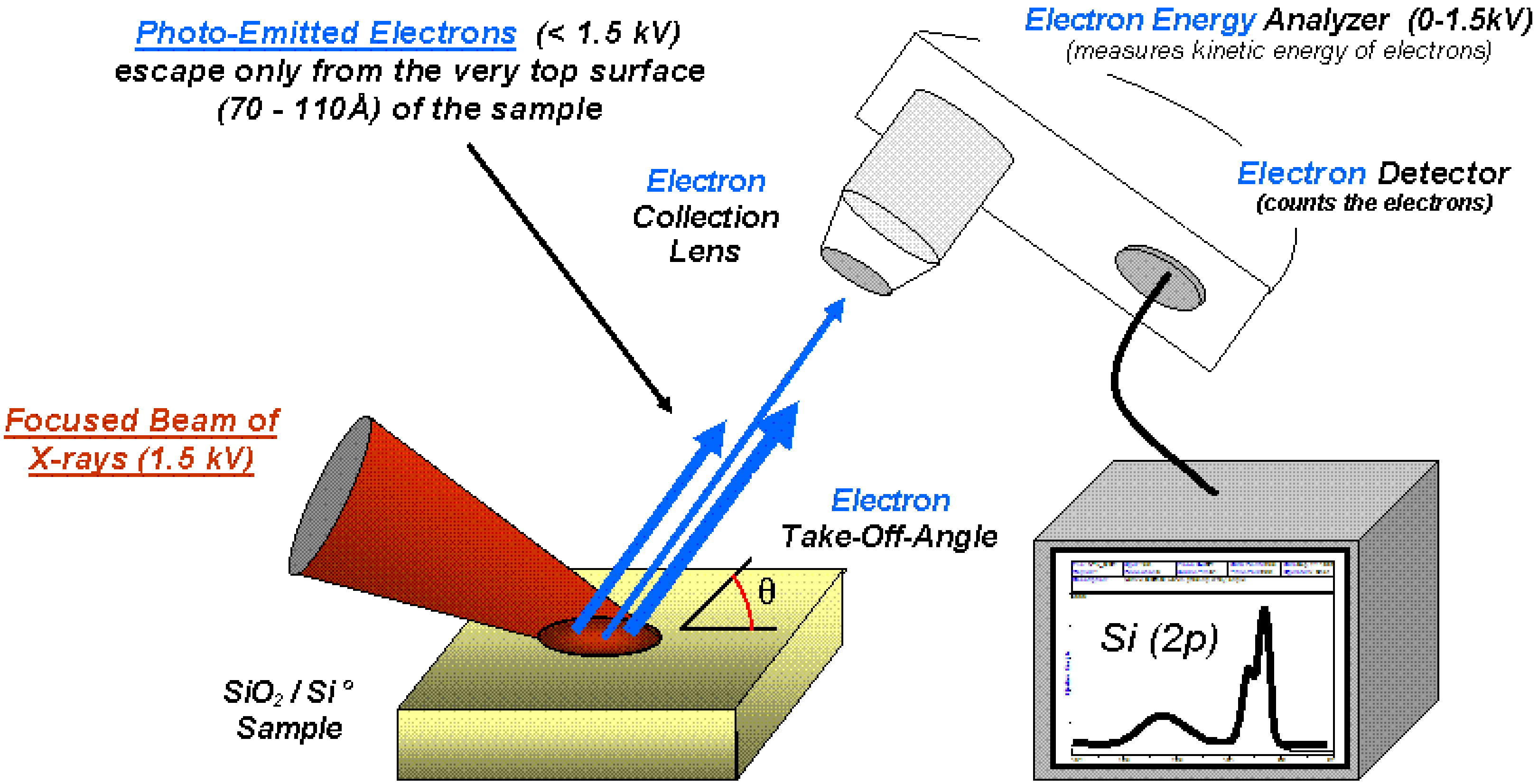


Photo-Emitted Electrons (< 1.5 kV)
escape only from the very top surface
(70 - 110Å) of the sample

Electron Energy Analyzer (0-1.5kV)
(measures kinetic energy of electrons)

Electron
Collection
Lens

Electron Detector
(counts the electrons)

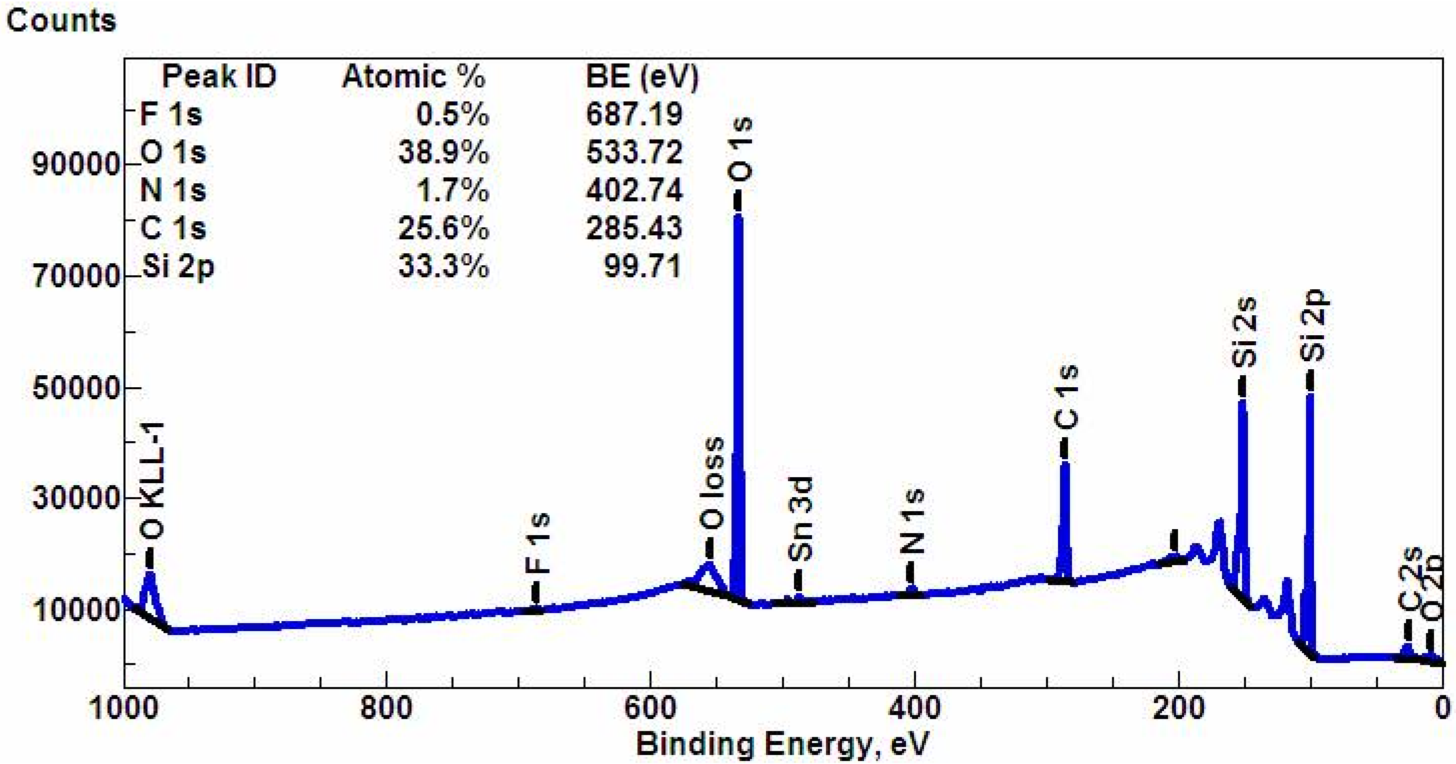
Focused Beam of X-rays (1.5 kV)

Electron
Take-Off-Angle

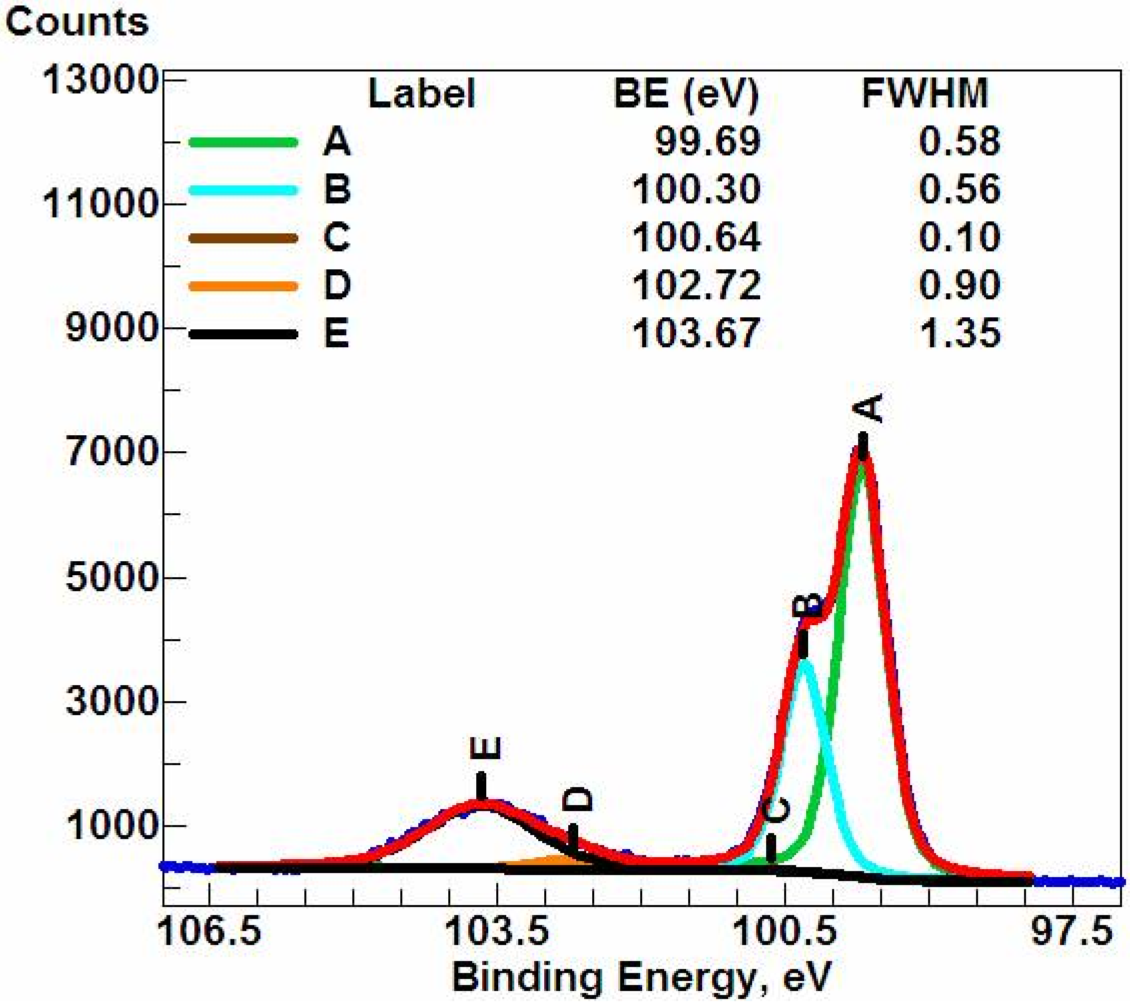
SiO_2 / Si°
Sample

Samples are usually solid because XPS requires ultra-high vacuum (<10^{-8} torr)

Si (2p) XPS signals
from a Silicon Wafer



Peak ID	Atomic %	BE (eV)
F 1s	0.5%	687.19
O 1s	38.9%	533.72
N 1s	1.7%	402.74
C 1s	25.6%	285.43
Si 2p	33.3%	99.71



Label	BE (eV)	FWHM
A	99.69	0.58
B	100.30	0.56
C	100.64	0.10
D	102.72	0.90
E	103.67	1.35