Auger Electron Spectroscopy AES

SURFACE ANALYSIS

MSE-351

Anna Igual Munoz

Reference book

D. Briggs, M.P. Seah

Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy

John Wiley & Sons (1994)

1. Introduction AES vs other techniques

2. Instrumentation

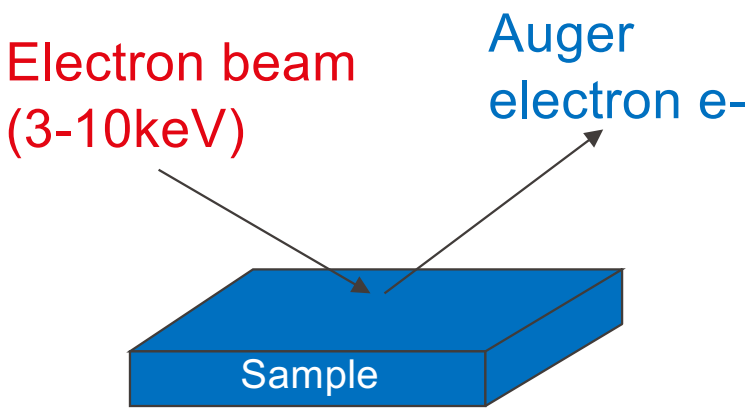
3. Spectral acquisition and interpretation

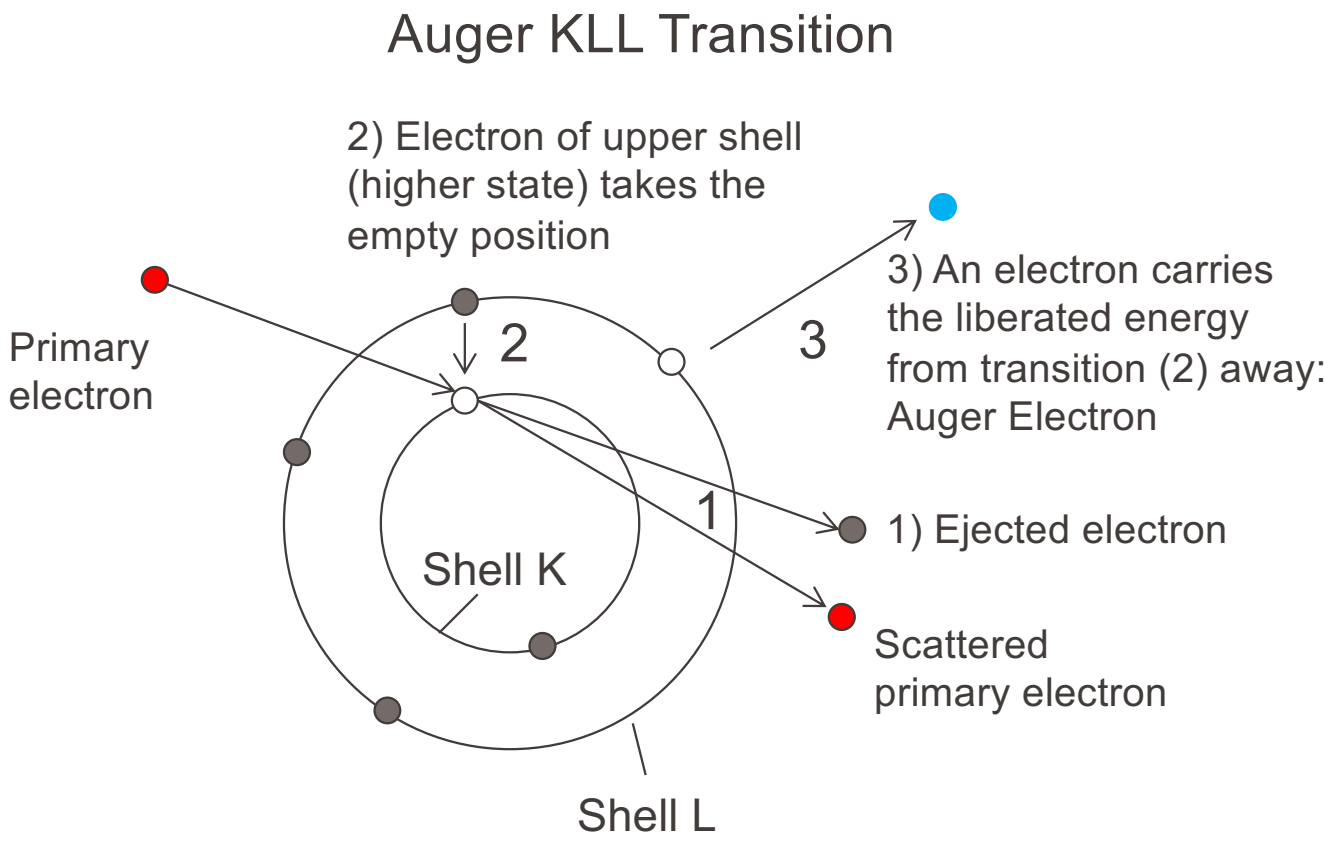
4. Quantification

5. Depth profiling

6. Applications

Principle of AES

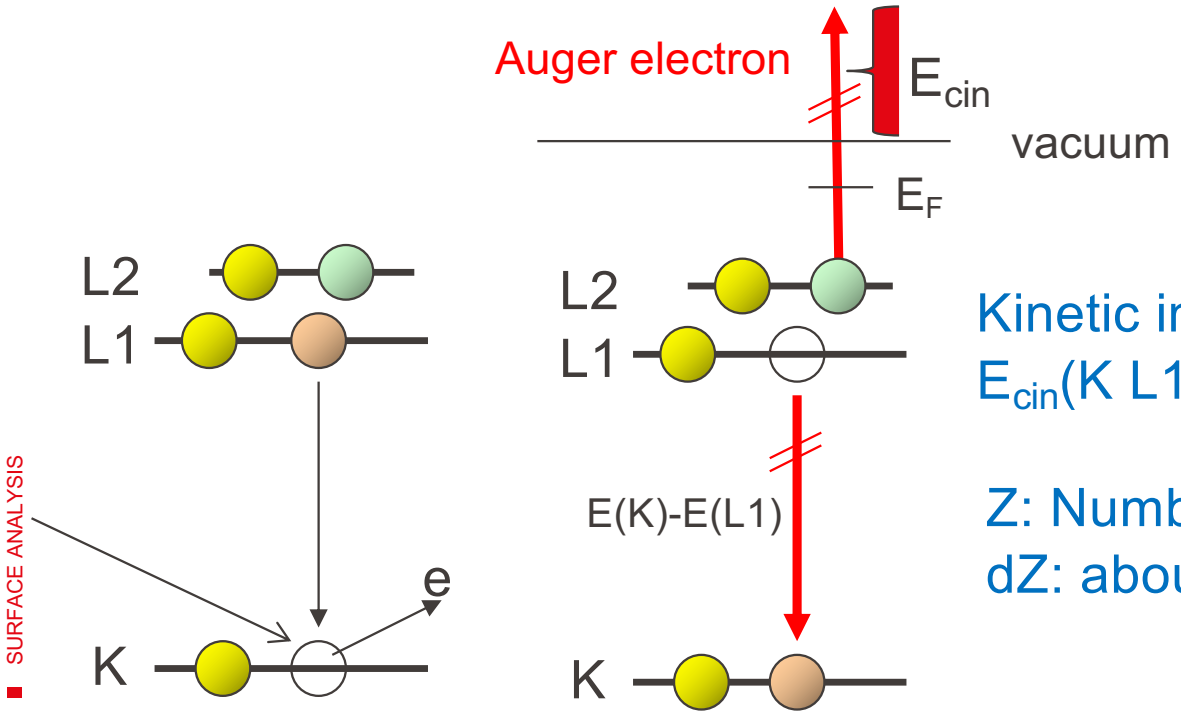




Analysis consists the spectrum of the electron as a function of their kinetic energy E_{kin}.

Auger electrons

Primary electron ejects electron in lower lying shell (here K-shell), an electron from a higher shell (here L-shell) makes a transition to the K-shell to fill the empty state. The liberated energy is taken by another electron from a higher shell (also L-shell in this case. Normally the two reacting electrons are from the same shell (same n), and leaves solid. This process is in competition with photon emission (fluorescence).



Kinetic in energy analyser (A):

$E_{cin}(K\ L1\ L2) = E_K(Z) - E_{L1}(Z+dZ) - E_{L2}(Z+dZ) - \Phi_A$

Z: Number of protons in nuclei

dZ: about 1/2

Auger Electron Spectroscopy (AES)

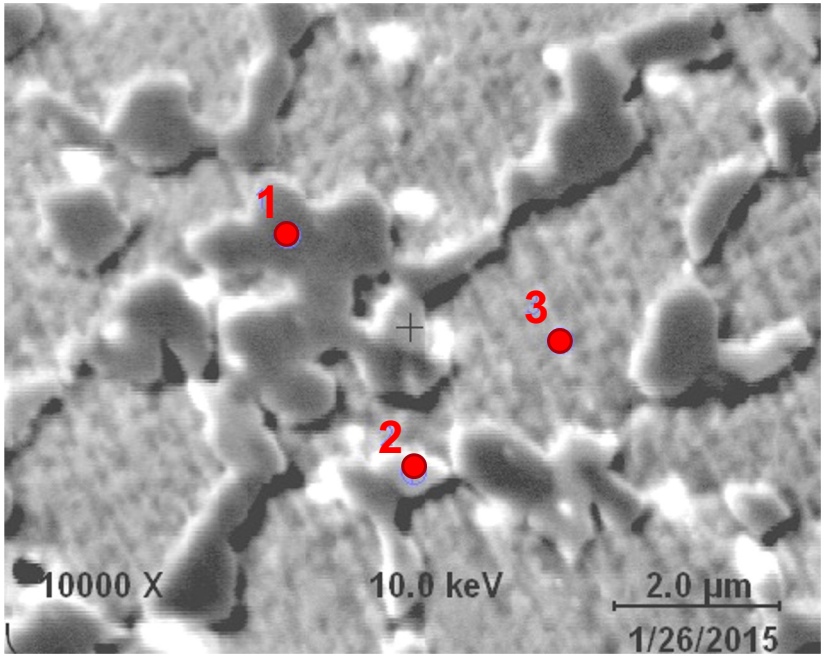
In relation to XPS

- Same vacuum requirements
- Similar electron energies and thus information depth
- Primary source: **electrons**
- Interpretation is more complicated, less popular than XPS
- Much finer primary beam → better lateral resolution (→ Scanning Auger Microscopy)
- More difficult to deal with insulating samples

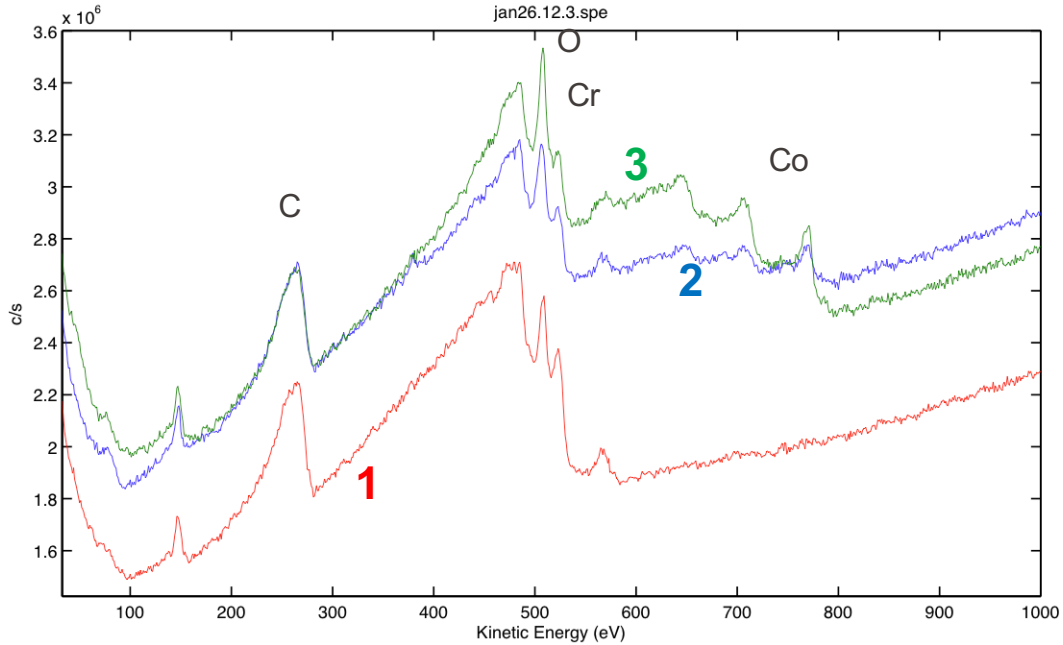
Discovery: P. Auger in 1923 (gas) and by Lise Meitner in 1922 (she did not make enough noise).
Harris 1967: Showed that AES is a good method for surface analysis.

Scanning Auger Microscopy (SAM)

Stellite alloy with CoCr metallic matrix and Cr and W carbide inclusions, corroded in sulphuric acid.

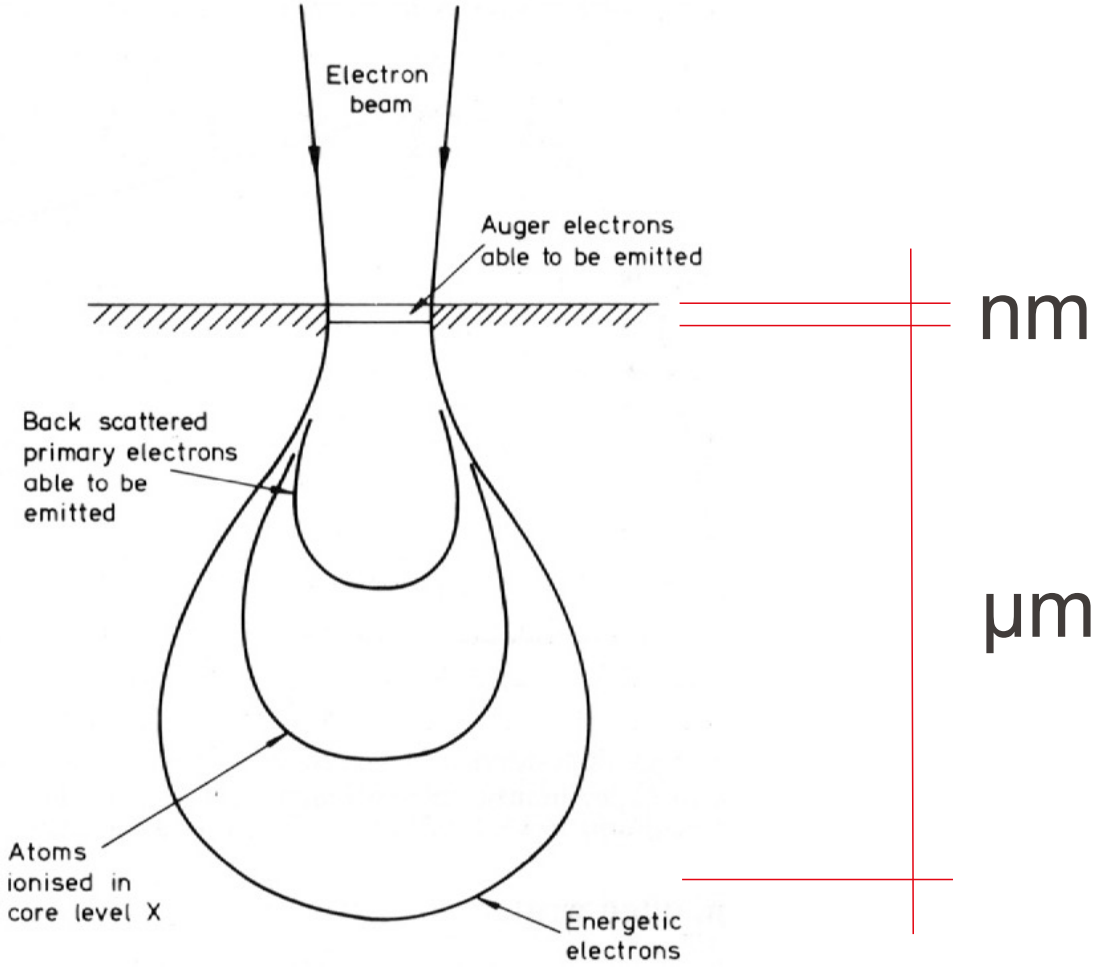


SEM image showing analysis points



AES spectra measured on single analysis points

Electron scattering in AES and EDX (Energy-dispersive X-ray spectroscopy



Ionised atoms may emit Auger electrons or X-Rays by fluorescence.

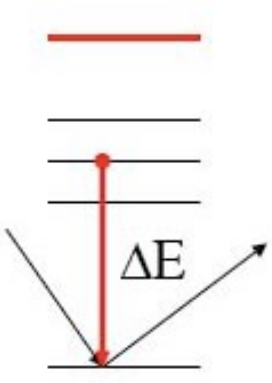
The mean free path of electrons is in the range of a few nanometres while X-rays can cross several µm.

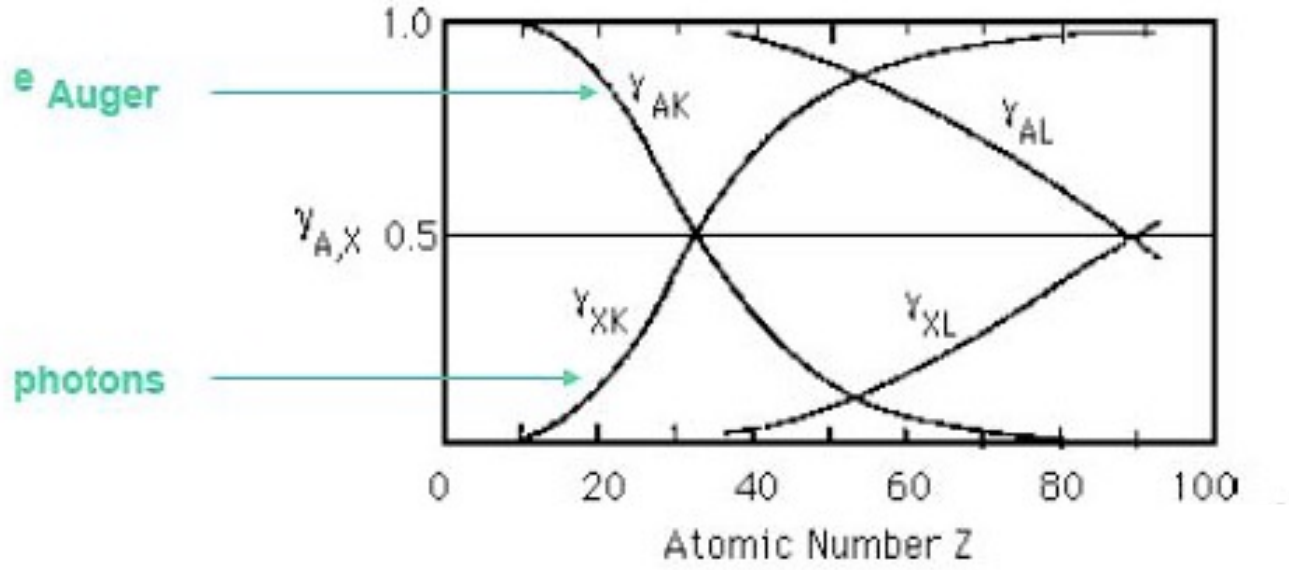
Thus, AES is surface sensitive while EDX (X-Rays emitted by fluorescence) measures much deeper.

Thickness of Auger electrons for different primary energies and mono-atomic materials

Depth (nm)	Primary energy (KeV)			
Z	**2.5**	**5**	**10**	**15**
Al(13)	0.12	0.4	1.25	2.4
Cu(29)	0.046	0.15	0.47	0.9
Au(79)	0.027	0.088	0.28	0.54

Auger vs. Fluorescence: transition probabilities





Auger: More likely for light elements, i.e. from Be to Ge.

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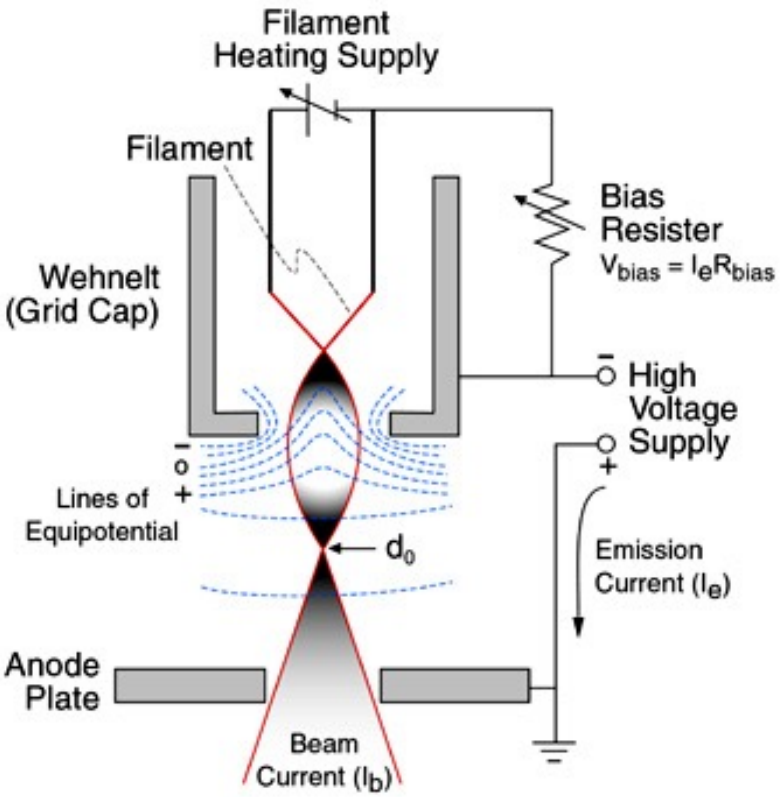
Electron sources for AES

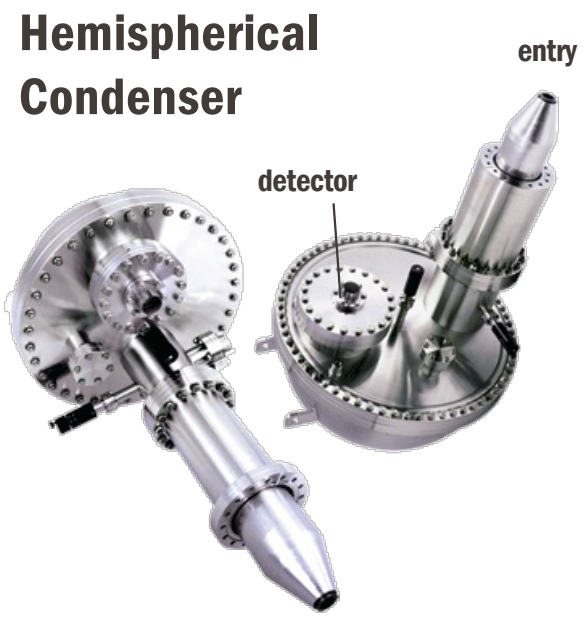


Types of filaments

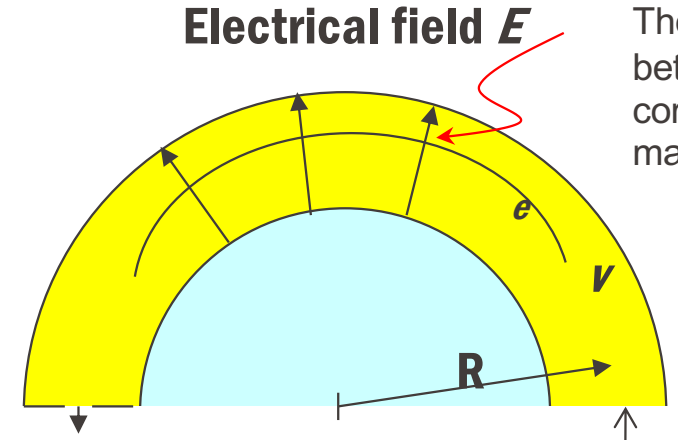
- Tungsten cathode source filaments (cost effective, beam ~2 A/cm^2)
- Lanthanum hexaboride (LaB6) cathodes (bright beams 100A/cm^2, narrow beams)
- Field Emission electron sources (very sharp tungsten tips with electrical fields >10^7 V/cm and tunnelling emission, brightest beams 10^3 to 10^6 A/cm^2). Very sensitive to contaminations.

The Concentric Hemispherical Analyser CHA

To measure the number of photo-ejeted electrons as a function of their energy



CHA: Concentric hemispherical analyser



The electric field is swept between zero and the value corresponding to the maximum E_{cin}.

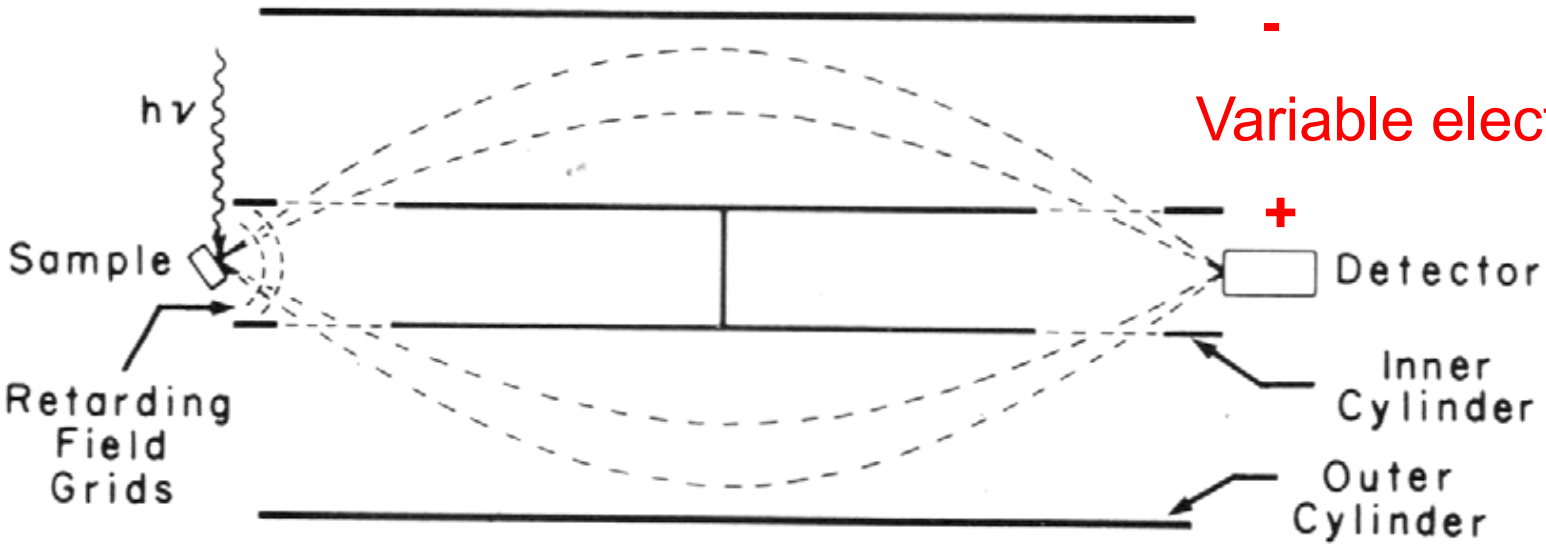
The electrons arriving at the detector (electron multiplier) have a kinetic energy of:

$$E_{cin} = \frac{1}{2} m v^2$$

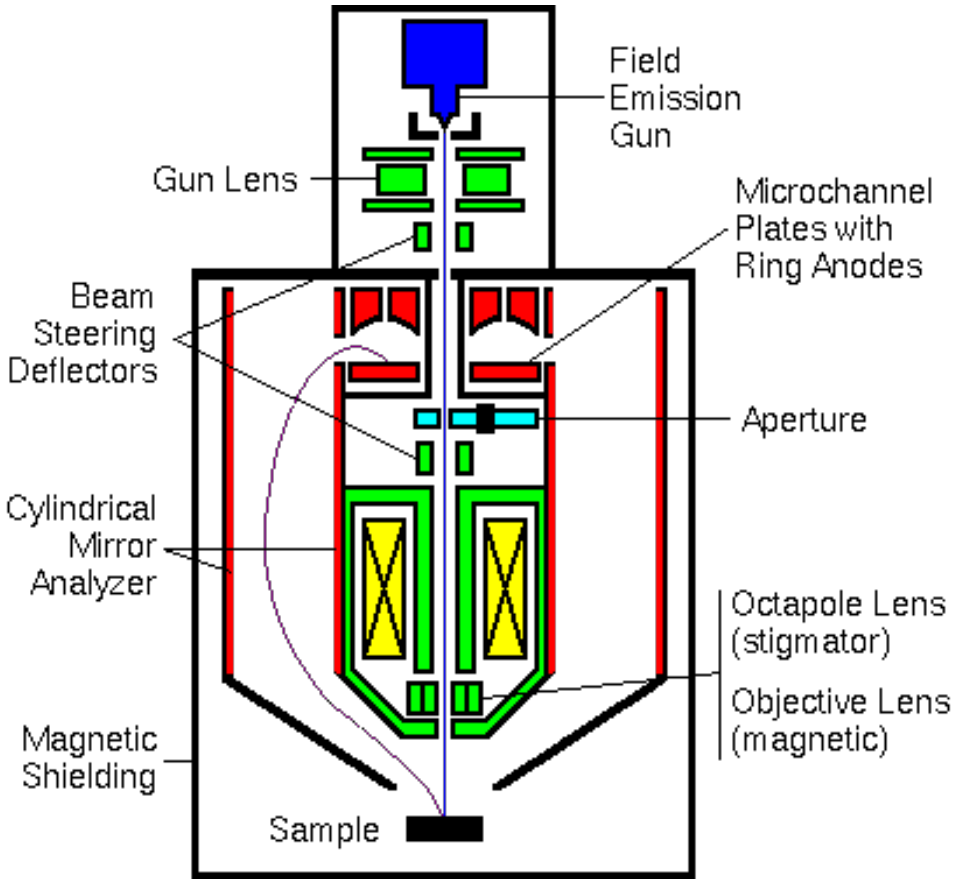
$$-eE = m_e \frac{v^2}{R}$$

$$E_{cin} = \frac{eER}{2}$$

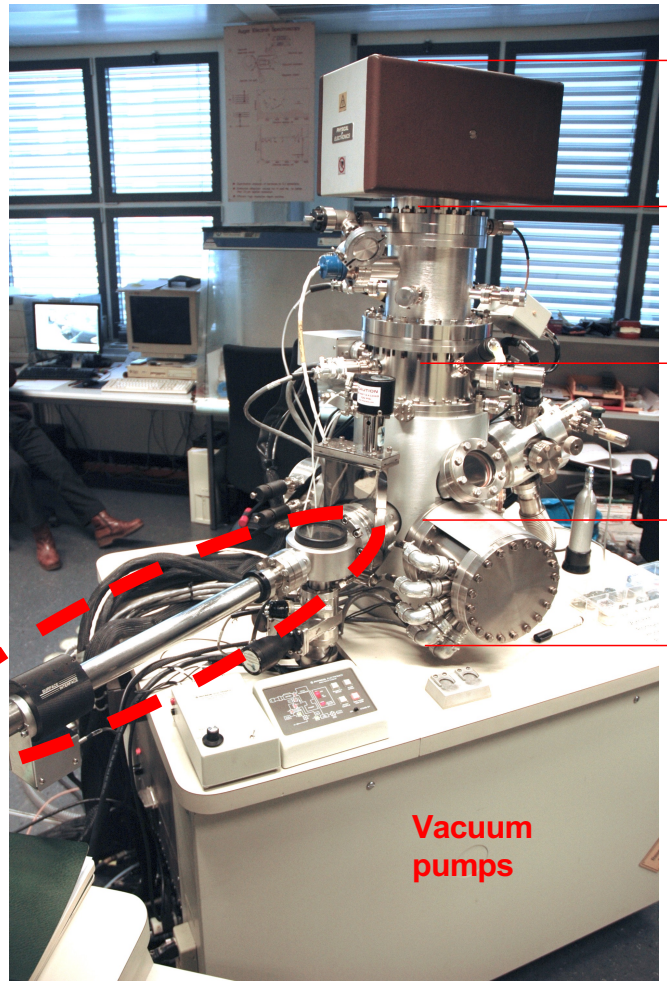
Cylindrical Mirror Analyser (CMA)



Co-axial assembly of electron gun and CMA analyser



AES PHI680 instrument of EPFL-MHMC



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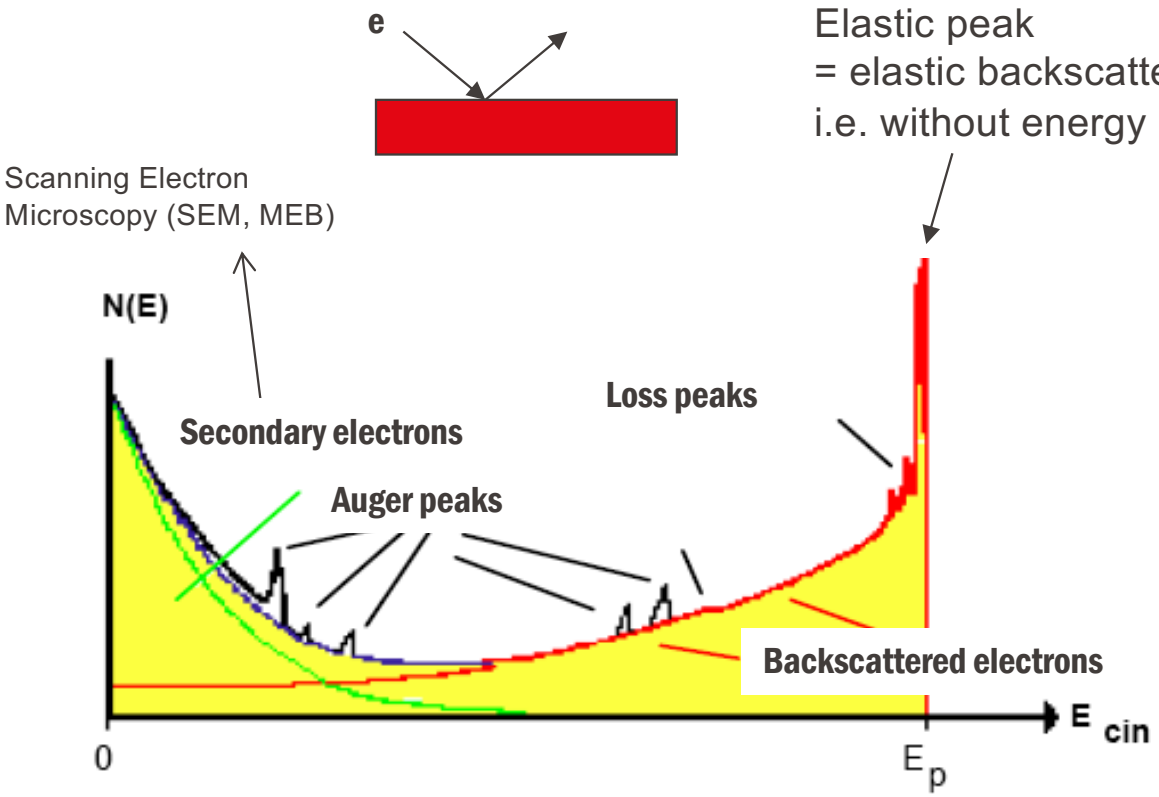
Secondary electron spectra

Emission of electrons after electron bombardment of solid material

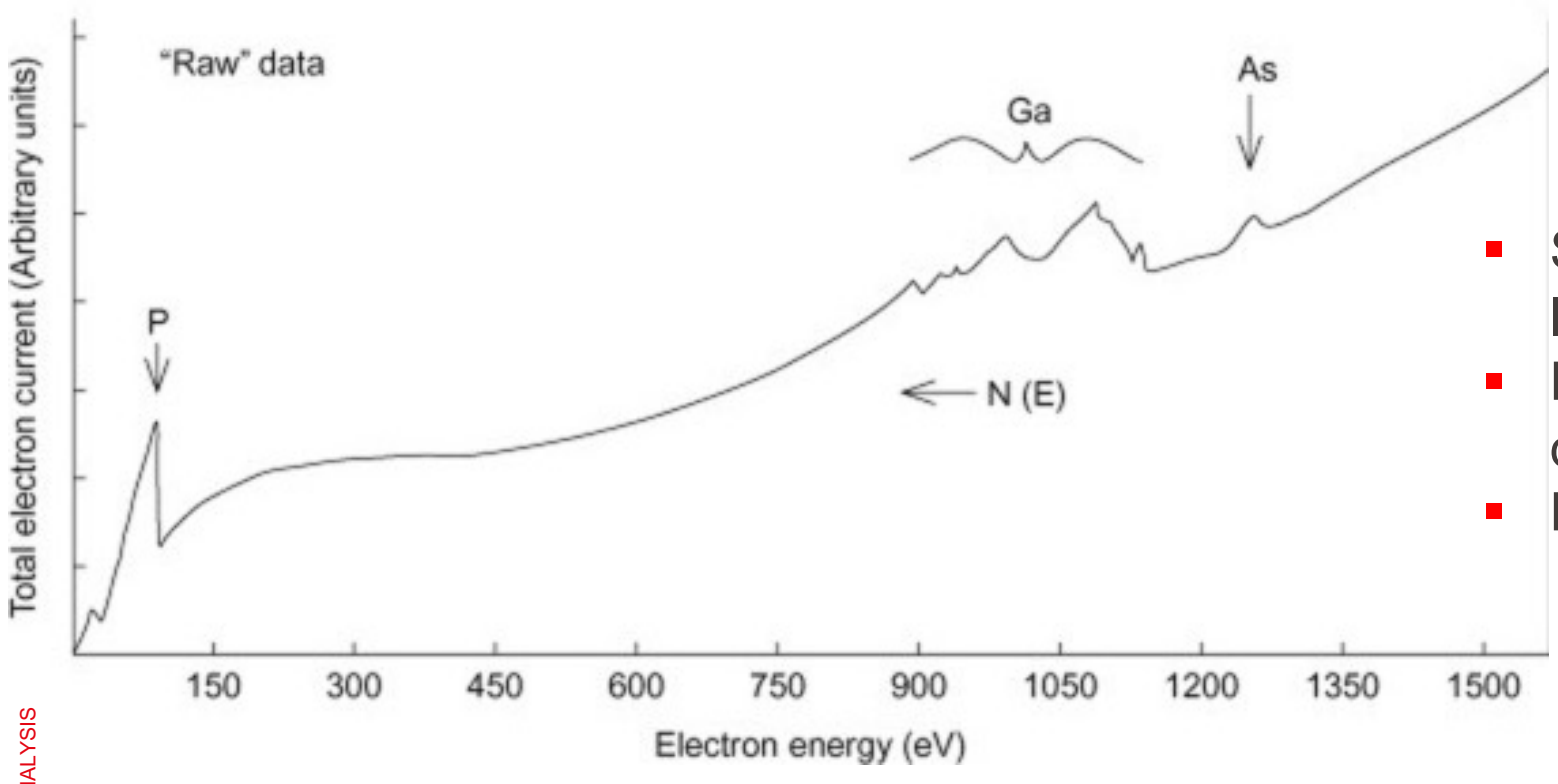


Two major contributions:

Green: Secondary electrons of low energy being formed by ionization of atoms.

Red: Backscattered electrons from the primary beam

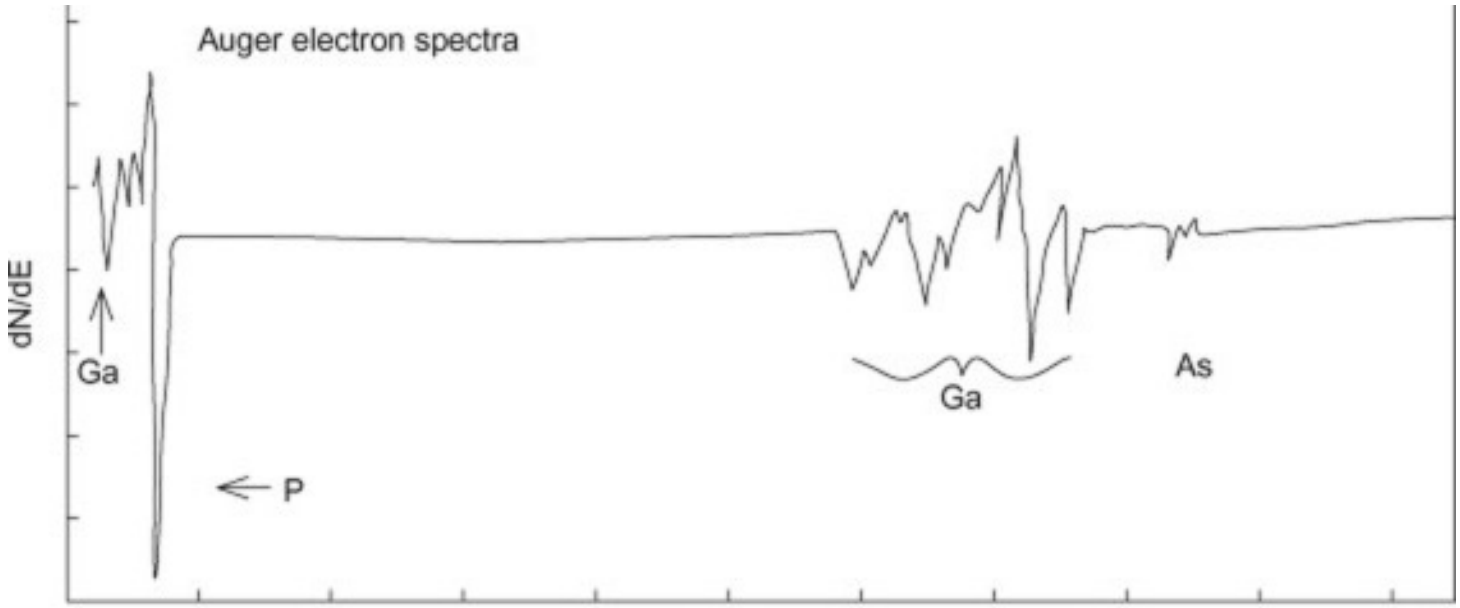
AES energy spectrum of a Gallium Arsenide surface



- Small peaks over a large background.
- Data interpretation difficult.
- P contamination.

Auger Electron Spectroscopy, H.L. Marcus, in Encyclopedia of Materials: Science and Technology, 2001

AES differential spectrum



- After differentiation dN/dE AES peaks are more pronounced and background is suppressed.

Auger Electron Spectroscopy, H.L. Marcus, in Encyclopedia of Materials: Science and Technology, 2001

AES peaks: nomenclature

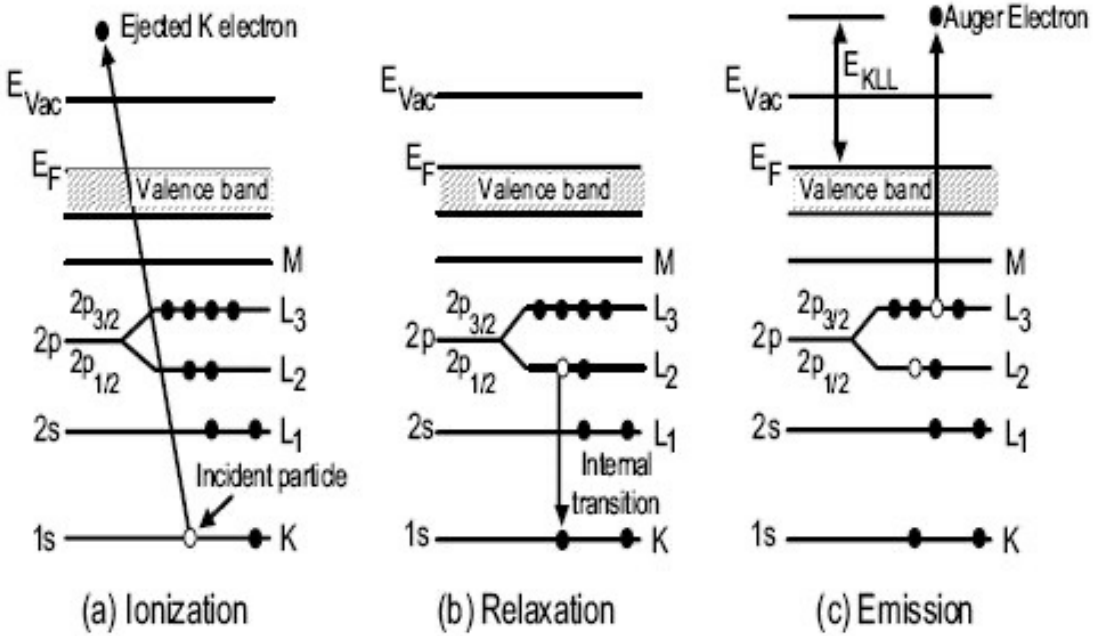
Elements can exhibit several AES peaks (depending on involved electrons) that have to be precisely defined.

This is done by considering the quantum numbers n, l and j = l + s, where s is the spin number (either +1/2 or -1/2).

Table 3.1 X-ray and spectroscopic notation

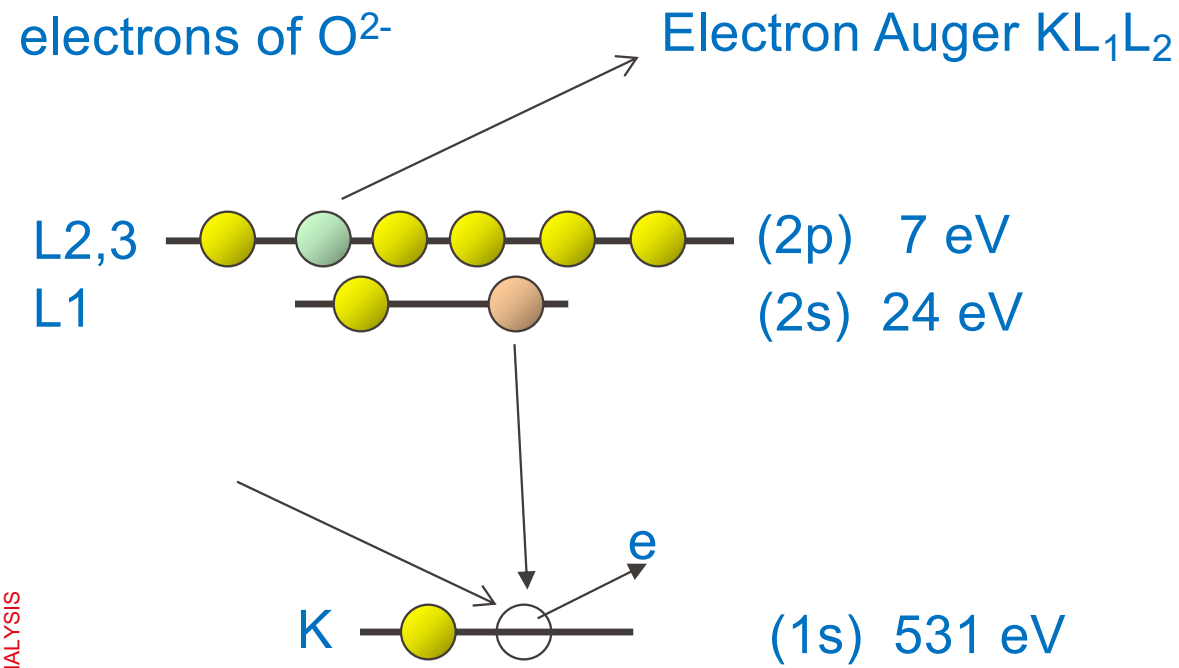
Quantum numbers					
n	l	j	X-ray suffix	X-ray level	Spectroscopic level
1	0	$\frac{1}{2}$	1	K	$1s_{1/2}$
2	0	$\frac{1}{2}$	1	L_1	$2s_{1/2}$
2	1	$\frac{1}{2}$	2	L_2	$2p_{1/2}$
2	1	$\frac{3}{2}$	3	L_3	$2p_{3/2}$
3	0	$\frac{1}{2}$	1	M_1	$3s_{1/2}$
3	1	$\frac{1}{2}$	2	M_2	$3p_{1/2}$
3	1	$\frac{3}{2}$	3	M_3	$3p_{3/2}$
3	2	$\frac{3}{2}$	4	M_4	$3d_{3/2}$
3	2	$\frac{5}{2}$	5	M_5	$3d_{5/2}$
	etc.		etc.	etc.	etc.

Auger process vs nomenclture



Quantum Numbers			Level Symbol	Auger Notation	XPS Notation
n	ℓ	j			
1	0	1/2	$^2S_{½}$	K	$1s_{1/2}$
2	0	1/2	$^2S_{½}$	L_1	$2s_{1/2}$
2	1	1/2	$^2P_{½}$	L_2	$2p_{1/2}$
2	1	3/2	$^2P_{3/2}$	L_3	$2p_{3/2}$
3	0	1/2	$^2S_{½}$	M_1	$3s_{1/2}$
3	1	1/2	$^2P_{½}$	M_2	$3p_{1/2}$
3	1	3/2	$^2P_{3/2}$	M_3	$3p_{3/2}$
3	2	3/2	$^2D_{3/2}$	M_4	$3d_{3/2}$
3	2	5/2	$^2D_{5/2}$	M_5	$3d_{5/2}$

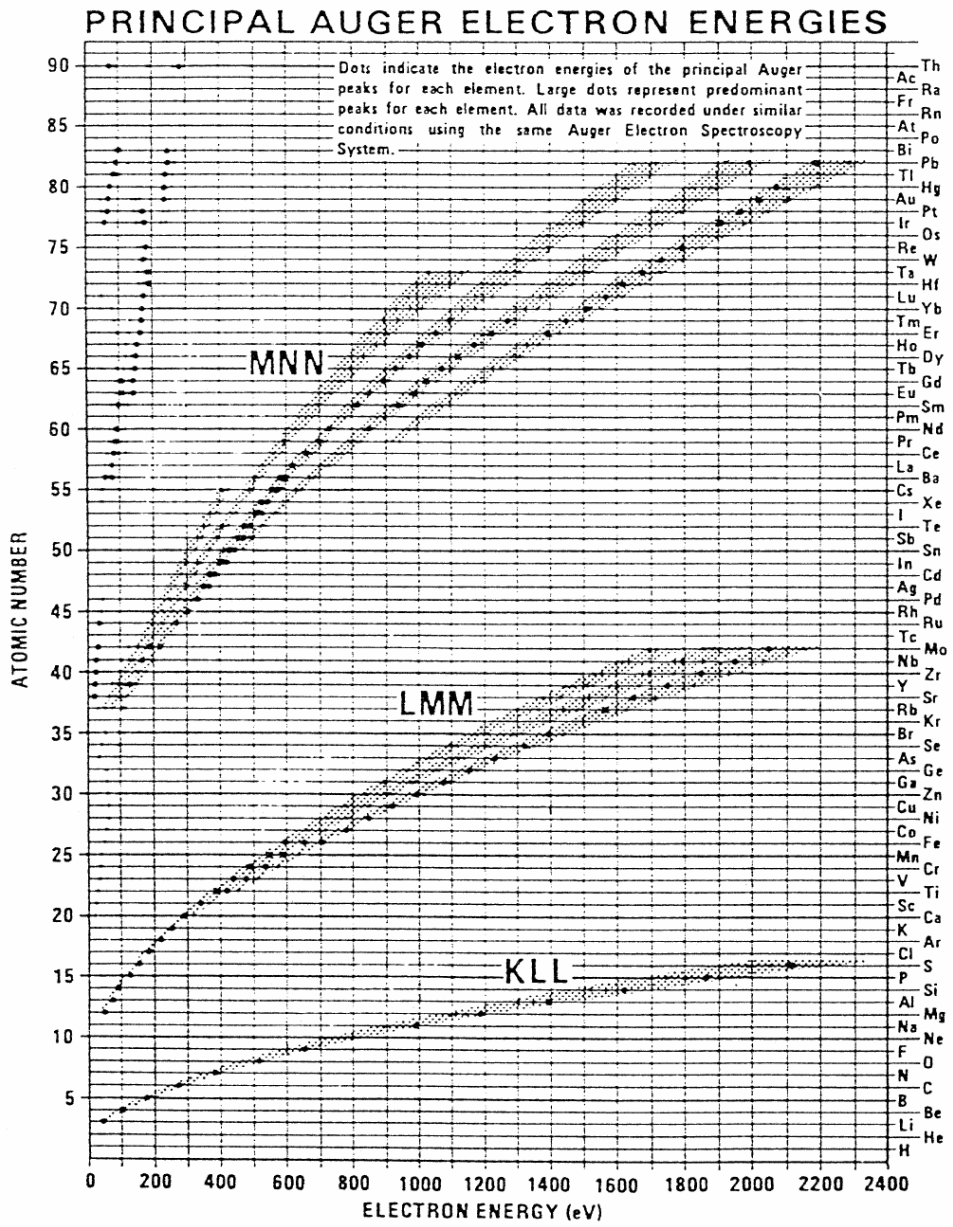
AES peaks nomenclature: example Oxygen (KLL peak)



Estimated energy:
531-24-7-Φ
Thus about 496 eV.

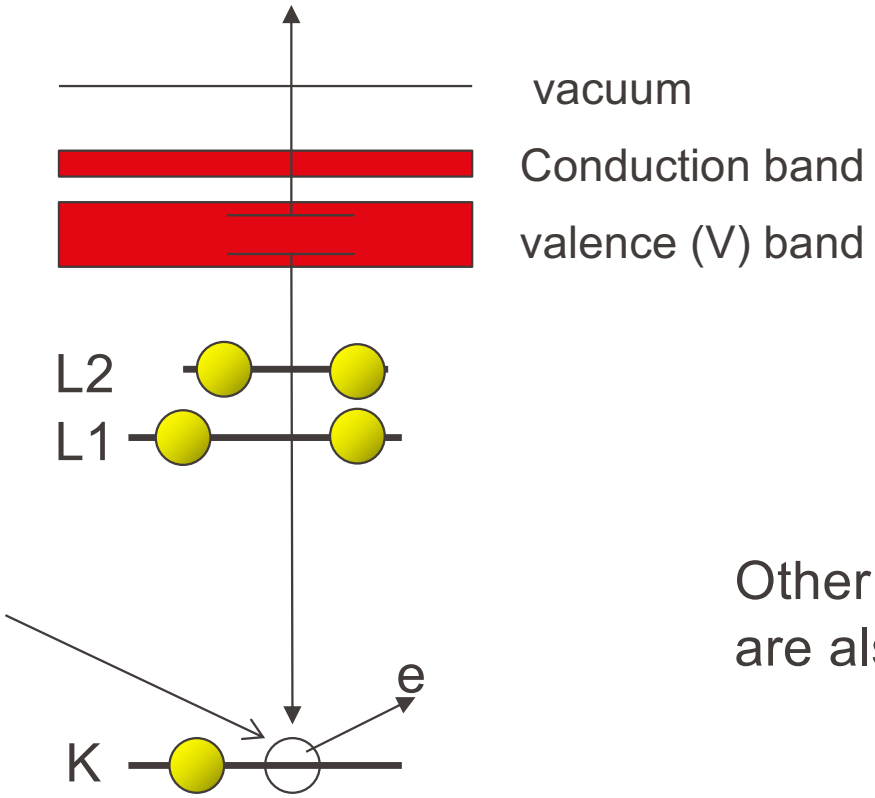
Measured 505 eV.

Not exactly exact because the energy levels are slightly different because one electron is missing when the Auger electron leaves.


PRINCIPAL AUGER ELECTRON ENERGIES
Dots indicate the electron energies of the principal Auger peaks for each element. Large dots represent predominant peaks for each element. All data was recorded under similar conditions using the same Auger Electron Spectroscopy System.
MNN
LMM
KLL
ATOMIC NUMBER
ELECTRON ENERGY (eV)
0 200 400 600 800 1000 1200 1400 1600 1800 2000 2200 2400
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
Th Ac Ra Fr Rn At Po Bi Pb Tl Hg Au Pt Ir Os Re W Ta Hf Lu Yb Tm Er Ho Dy Tb Gd Eu Sm Pm Nd Pr Ce La Ba Cs Xe I Te Sb Sn In Cd Ag Pd Rh Ru Tc Mo Nb Zr Y Sr Rb Kr Br Se As Ge Ga Zn Cu Ni Co Fe Mn Cr V Ti Sc Ca K Ar Cl S P Si Al Mg Na Ne F O N C B Be Li He H

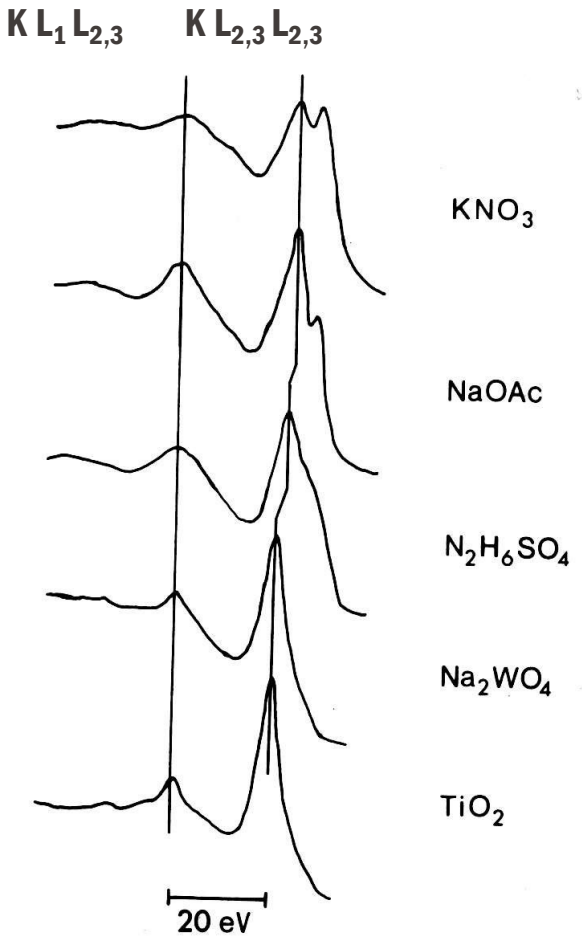
Auger electrons of the valence band

Example of the transition KVV



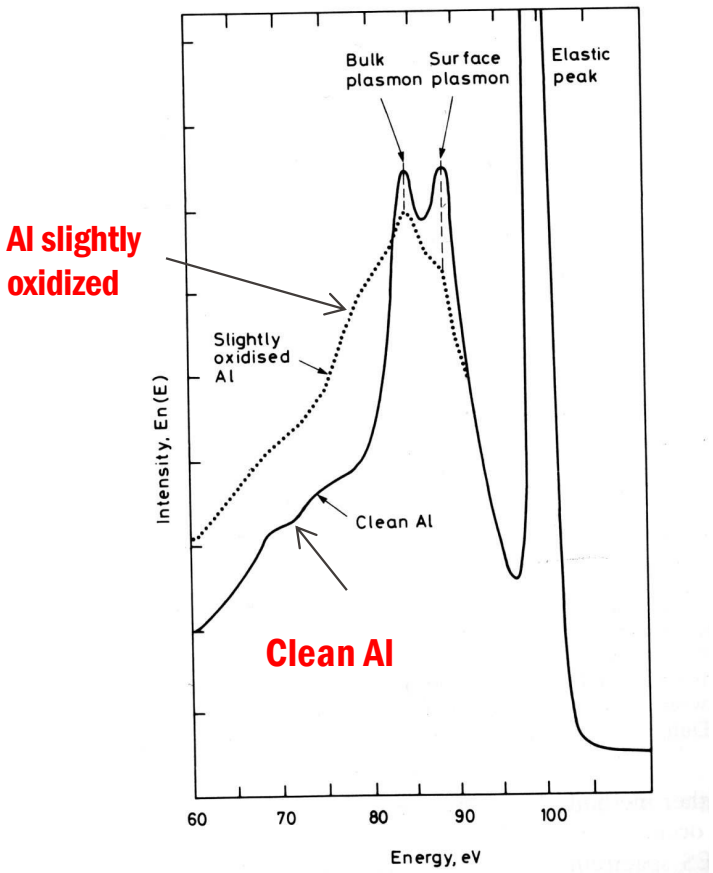
Other transitions, ex. LVV, are also possible

Chemical information in AES: example O_{KLL}



Valence electrons: $L_{2,3}$ The valence electrons are very sensitive to chemical bonds.

Loss peaks du to plasmon oscillations Al_{LMM}



Interaction with electrons of the conduction band. One can differentiate bulk and surface plasmons.

The observation of plasmons is a clear sign that the sample is metallic.

The graph shows the plasmon peaks below the peak of elastically backscattered electrons (with a small primary energy)

The plasmon peaks are also present below Auger transitions.

Calibration of the energy scale

- AES peaks are usually broad and therefore energy calibration is less stringent.
- For energy calibration the sample is illuminated by an electron beam of low known primary energy (typically 1keV) and the elastic backscattering peak measured by the analyzer is set to the primary energy.

Note that with CMA the distance sample surface to analyzer influences the measured kinetic energy, so the distance is adjusted in order to make primary and backscatter peak energies coinciding.

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2 methods for quantification

1. Calculation of absolute concentrations using the Peak-to-Background approach (N(E) spectra)
   S. Mischler, H.E. Bishop, SURFACE AND INTERFACE ANALYSIS, VOL. 17, 315-319 (1991)

2. Calculations using Relative atomic sensitivity factors as in XPS (dN(e)/dE spectra)

The intensity I_A of an AES peak

$$I_A = I_P C_A \sigma_t \gamma_A R \lambda \cos \Theta_o \sec \Theta_i T D$$

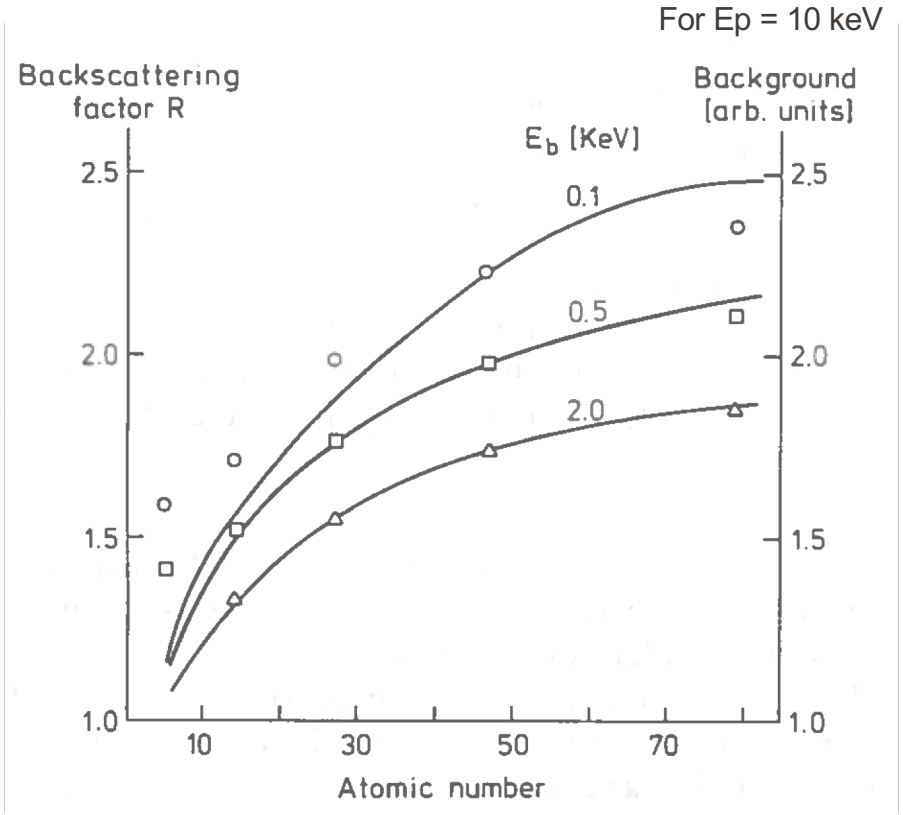
I_A: Auger electron current for element A
I_P : Primary electron beam current
C_A: Atomic concentration of element A (atoms per unit volume)
σ_t : Ionization cross-section for primary beam energy E_p
γ_A: Probability of Auger emission for given transition
R : Back-scattering factor for Auger production from a level with binding energy E_b, for an electron beam angle of incidence Θ_I (vs surface normal)
$\lambda(E_k)$: Inelastic mean free path of an electron with kinetic energy E_k
Θ_o: Angle of emission of the Auger electron (vs surface normal)
$T(E_k)$: Transmission function of the analyser
$D(E_k)$: Efficiency of electron detector

The intensity I_A of an AES peak: simplified

$$I_A = kI_p C_A R(Z, \Theta_i)\lambda \cos \Theta_o \sec \Theta_i$$

I_A: Auger electron current for element A
k: constant for given E, Auger transition and instrument settings
I_P : Primary electron beam current
C_A: Atomic concentration of element A (atoms per unit volume)
R : Back-scattering factor for Auger production from a level with binding energy E_b, for an electron beam angle of incidence Θ_I (vs surface normal)
$\lambda(E_k)$: Inelastic mean free path of an electron with kinetic energy E_k
Θ_o: Angle of emission of the Auger electron (vs surface normal)

AES background at 2keV as calibration of R



$$I_A/B = \beta_A \lambda C_A$$

B: background level at 2 keV (for Ep=10keV)

β_A: constant for a particular transition, Ep and instrument. Does not depend on sample composition!

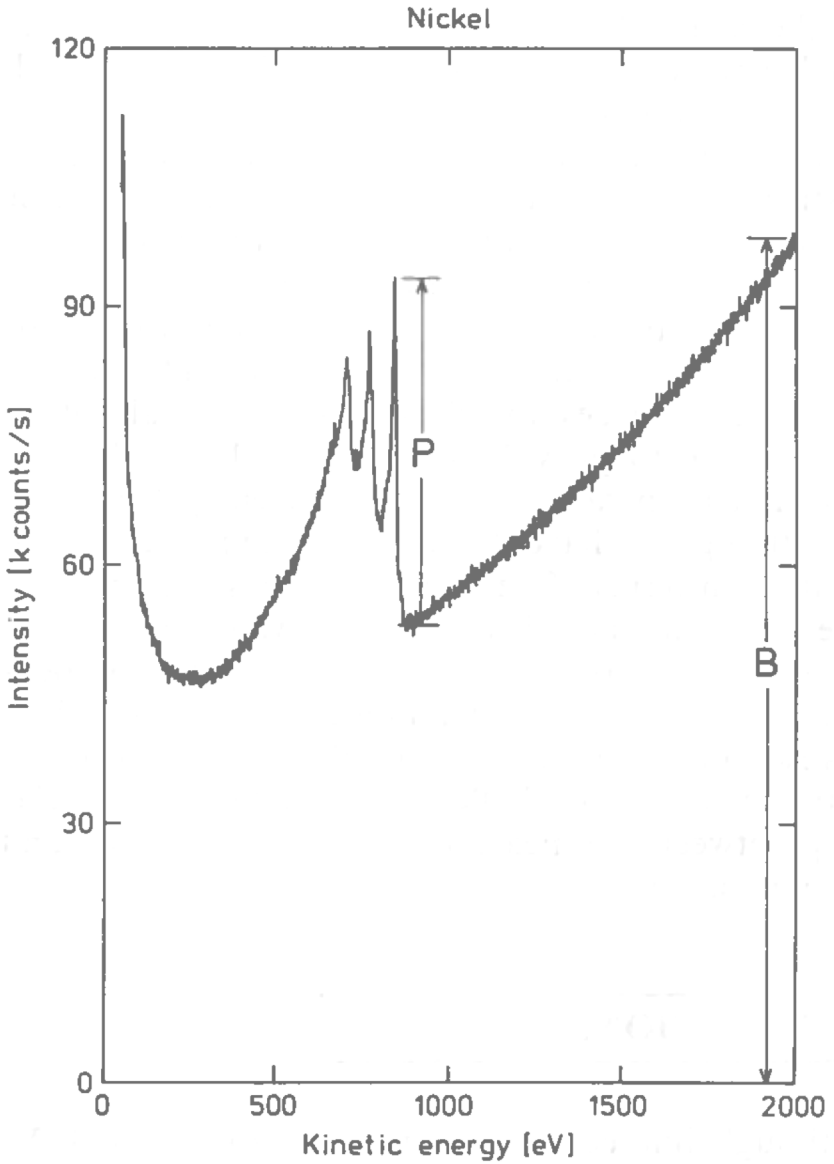
Example: Nickel

$$I_A/B = P/B = \beta_A \lambda C_A$$

$$C_A = P/(B\ \beta_A \lambda)$$

β_A needs to be calibrated

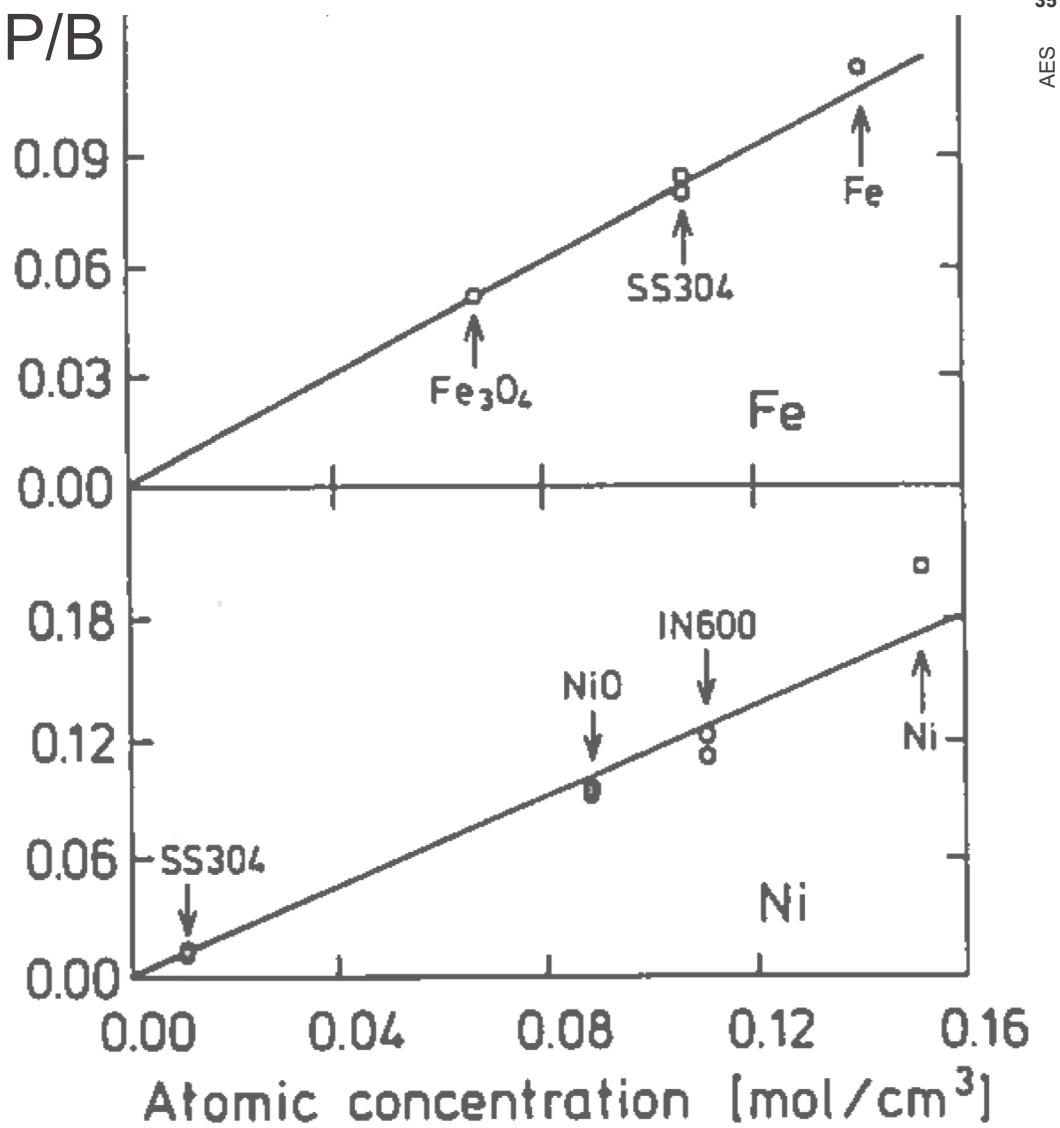
λ can be calculated as in XPS



Calibration of β_A for iron and nickel

Quantification using P/B ratio:

+ direct determination of absolute atomic concentrations
+ independent on sample composition
+ no need to consider other element
- B at 2keV often overlap with AES peaks and thus not representative of backscattering factor R
- Calibration must be made for each instrument



Quantitative analysis (homogeneous solids)

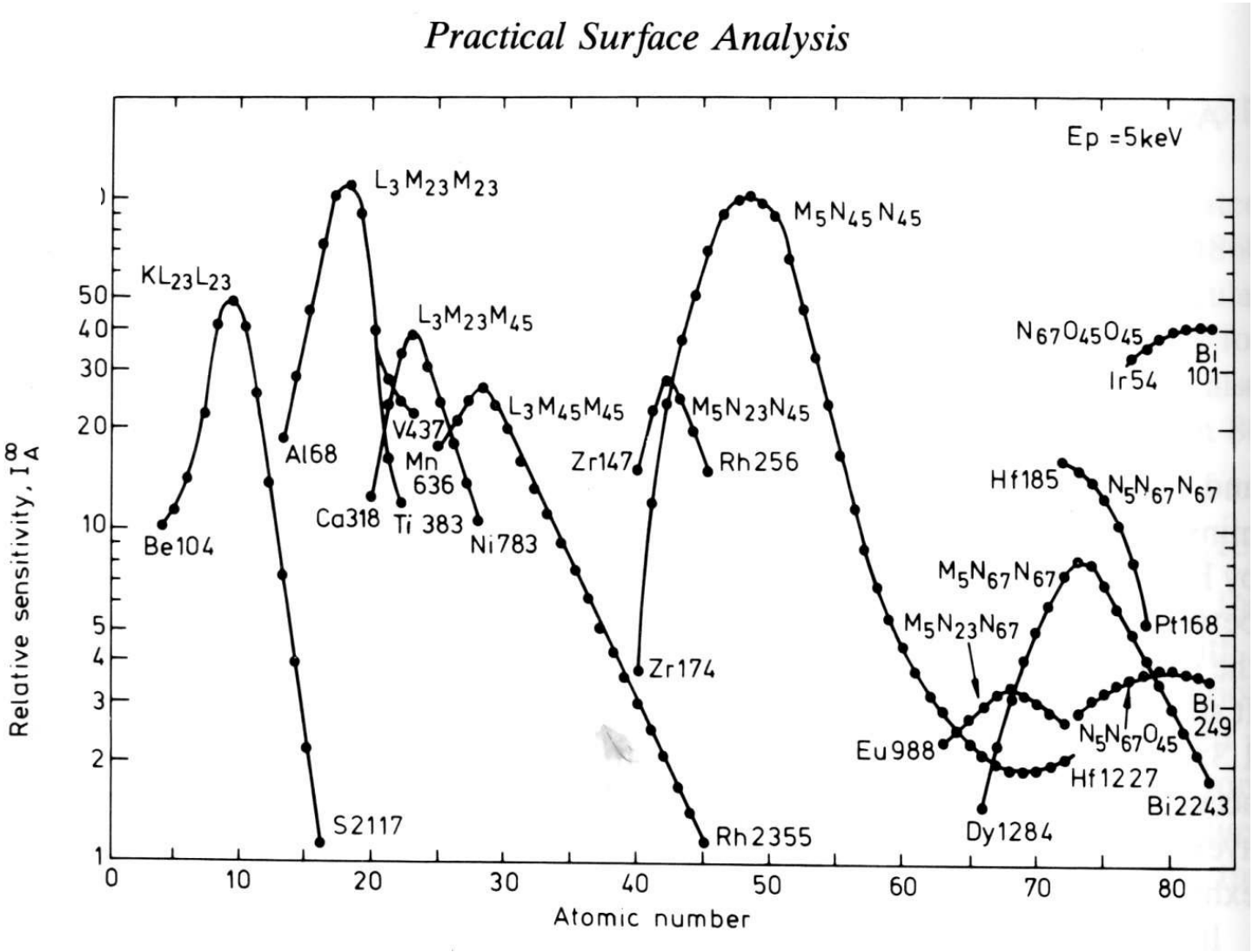
$$c_A = \frac{I_A / S_A}{\sum_{k=1}^{n} I_k / S_k} = \frac{I_A / RSF_A}{\sum_{k=1}^{n} I_k / RSF_k}$$

Relative atomic **S**ensitivity **F**actors (RSF)

c_A: relative concentration

- The RSF are instrument specific, essentially because of different T and D factors.
- The RSF are highly matrix dependent
- RSF do not take into account backscattering effects when an element is present in a different environment than the one used for calibration.
  Example: C is calibrated on graphite and thus adventitious carbon contaminations are overestimated when materials of higher atomic number (larger backscattering) are analysed.

AES atomic sensitivity factors



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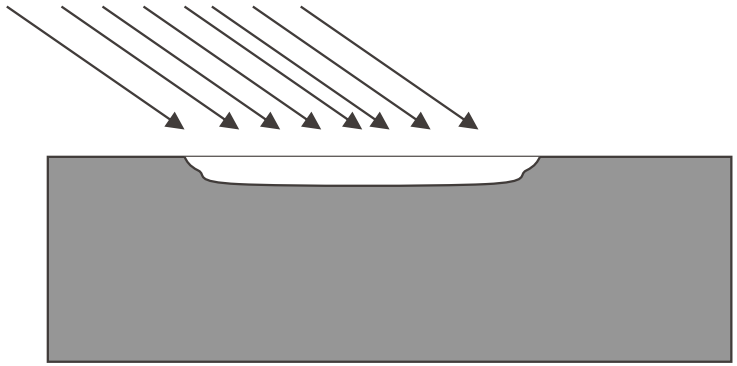
AES is usually combined with ion etching for depth profiling purposes

Erosion of the sample surface by an ion beam (ex Ar+ ions)



- 3 nm/min

The etching rate is about constant in an homogeneous solid. With simultaneous XPS spectra -> depth profile.

Sometimes the ionic bombardment changes the surface composition!

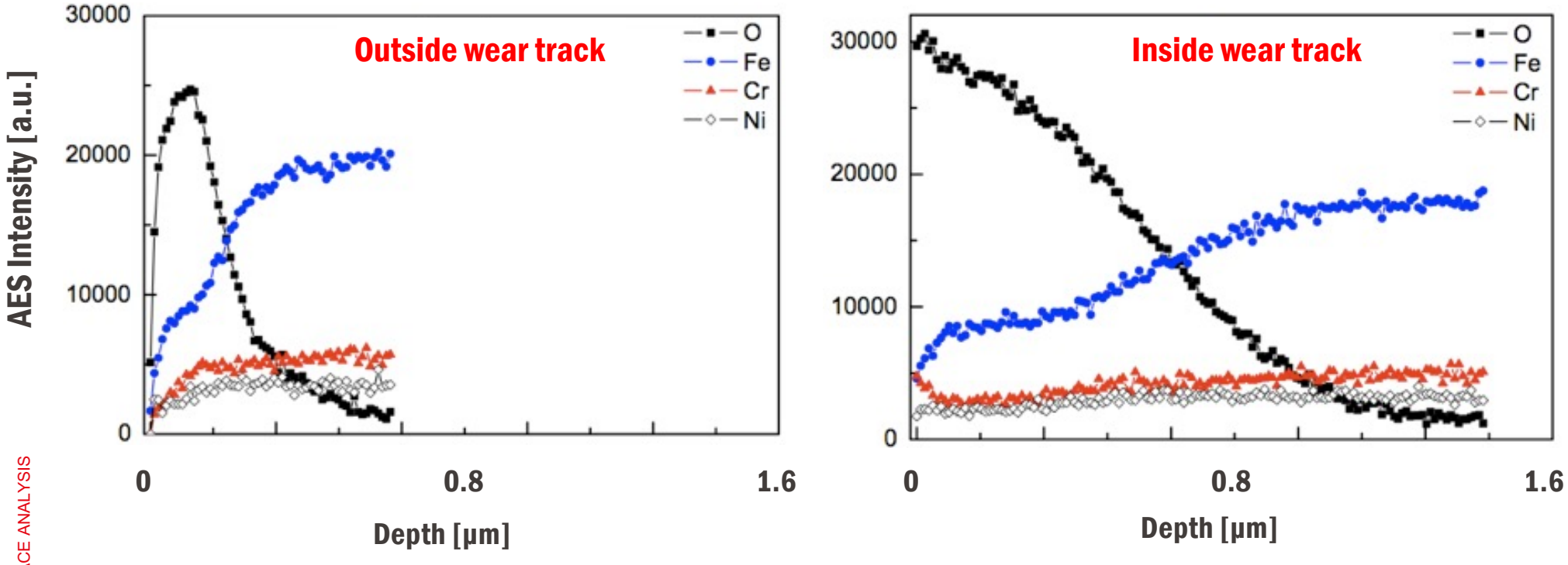
Sputter rates

- Sputter rates are calibrated using standard think film of known thickness such as Ta_2O_5 or SiO_2 films
- They are usually expressed an thickness of removed material per unit time sputtering, i.e. nm/min
- The sputter rate depends on type of ions, their energy and they current

Sputter rated depend on materials

Material	Relative sputter rate at 4keV Ar+
Ta_2O_5	1
Si	0.9
SiO_2	0.9
Pt	2.2
Cr	1.4
Al	1
Au	4.1

Depth profiling on an oxide formed on stainless steel worn samples in pressurized high temperature water



Oxide film thickness and composition is affected by rubbing: thicker film on sample areas subject to rubbing.

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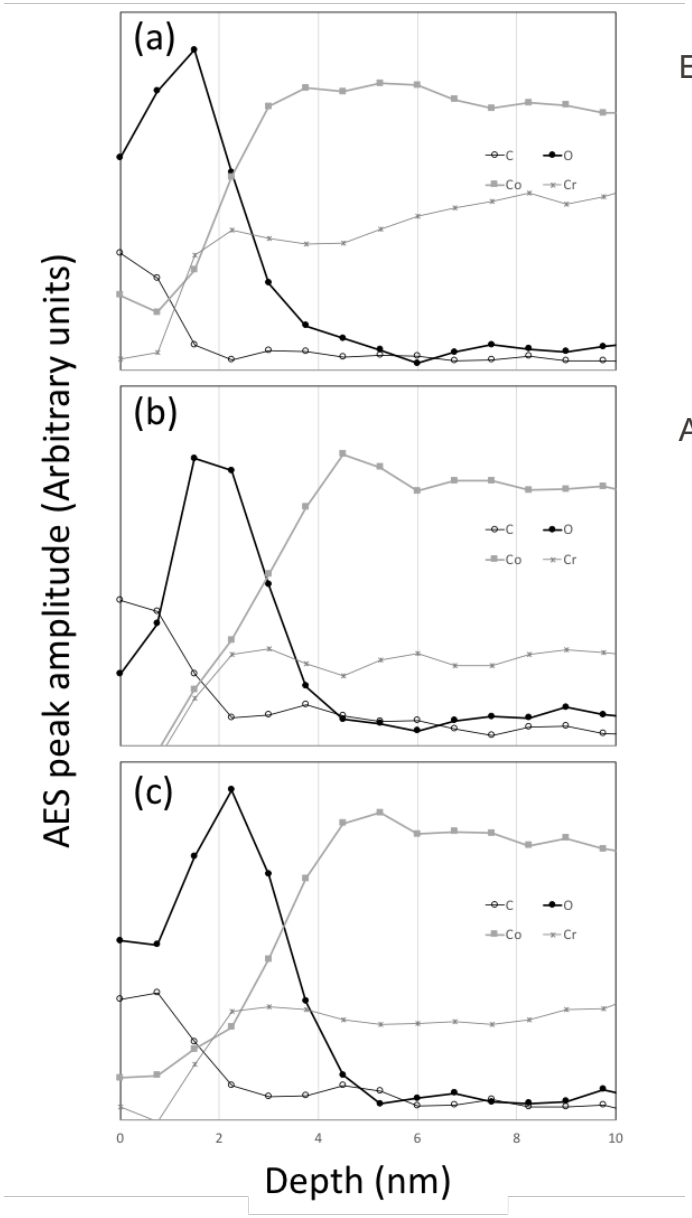
Applications fields of AES

- Thin film research
- Microelectronics
- Corrosion / Tribology
- Alloys
- ….

- Highly complementary technique to XPS

AESprofile of a CoCrMo alloy after different sterilization processes

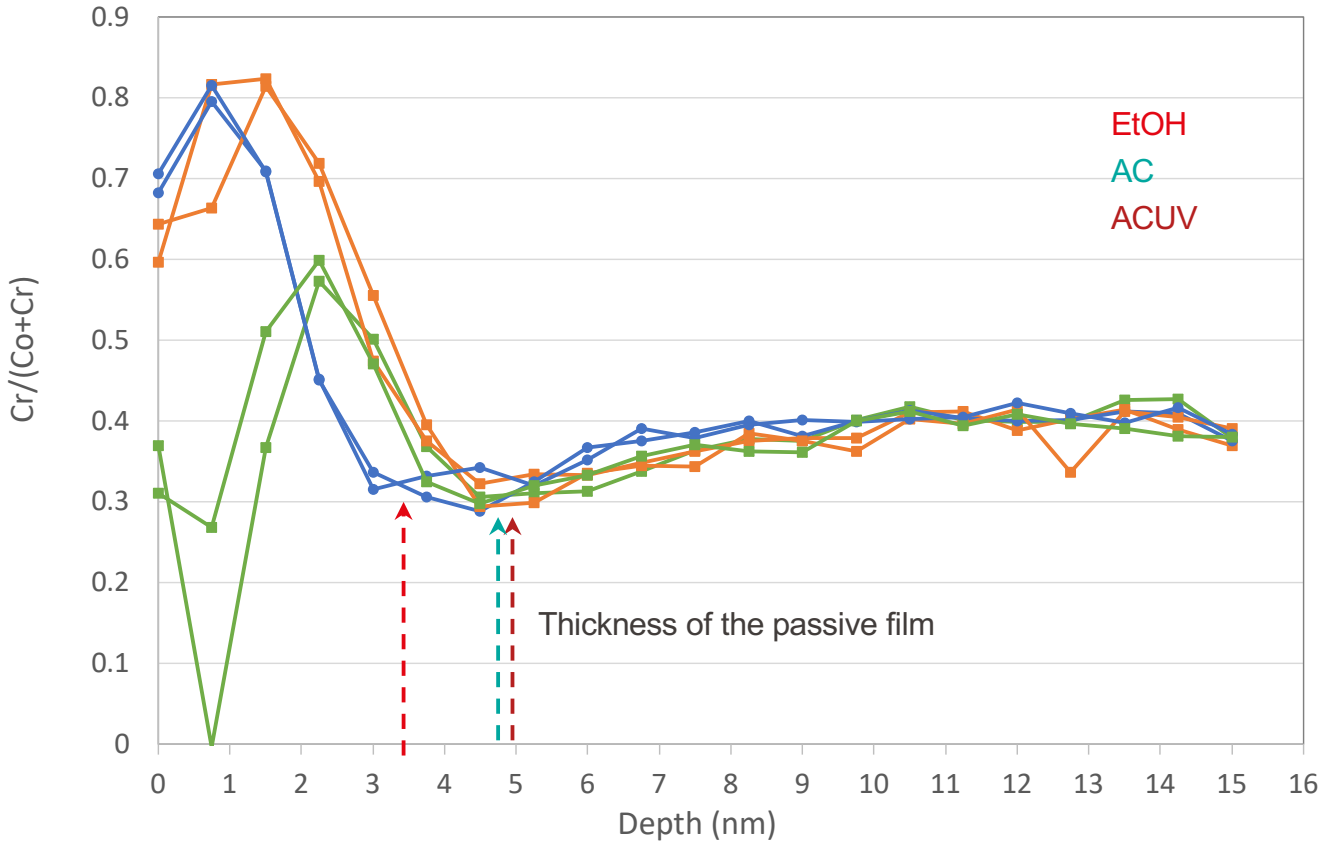


Ethanol

AC (Autoclave)

AC-UV (Autoclave + Uvlight)

Chromium to Cobalt ratio as a function of sputter depth



Comparison AES and XPS

- Background / peak width: no influence of the source!!
- Kinetic energy: Independent of the primary e-beam energy
- AES is very strong for the analysis of metallic surfaces
- AES is more complex than XPS, and potentially contains more information. However, the interpretation is more difficult
- Imaging of AES has much better lateral resolution.