



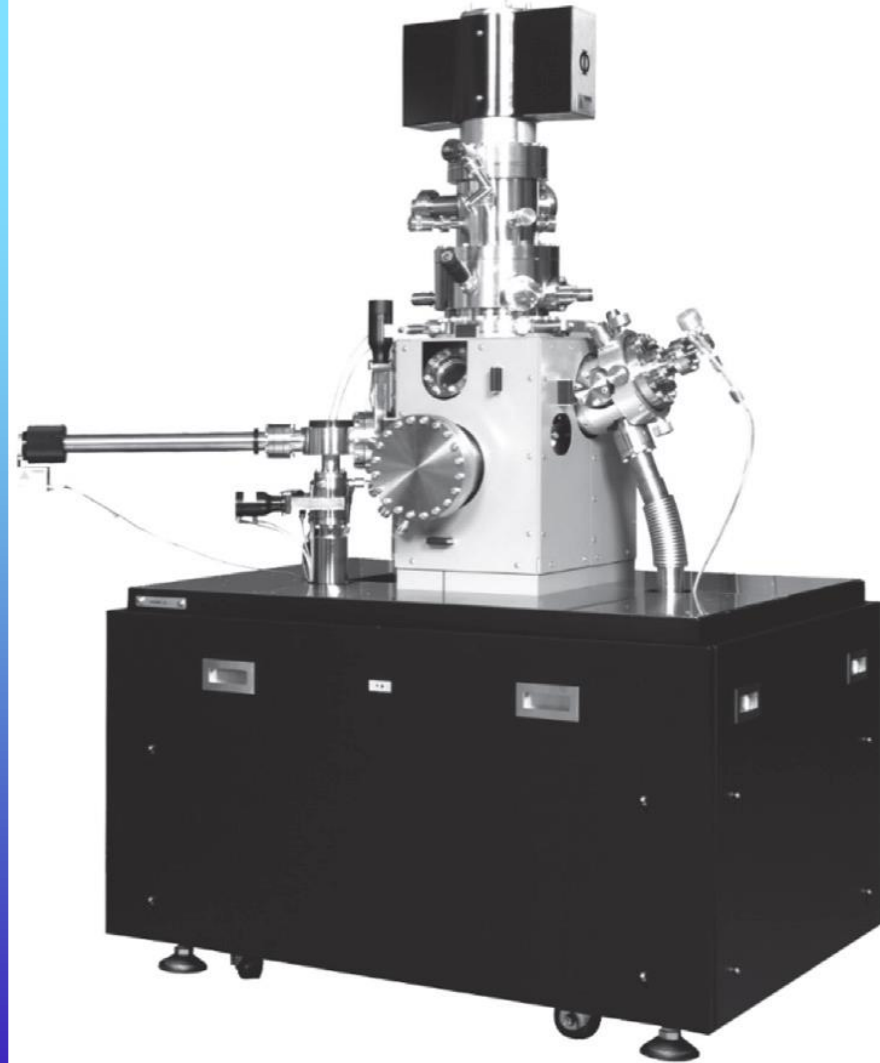
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Auger Electron Spectroscopy(AES)



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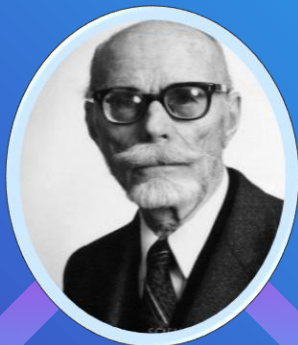
Application

What AES data is and how it is used

AES EVOLUTION

1923

Lise Meitner



1953

J. J. Lander



1969

Paul Palmberg



1925

Pierre Auger



1968

Andrew Harris



HOW DO WE DO IT?

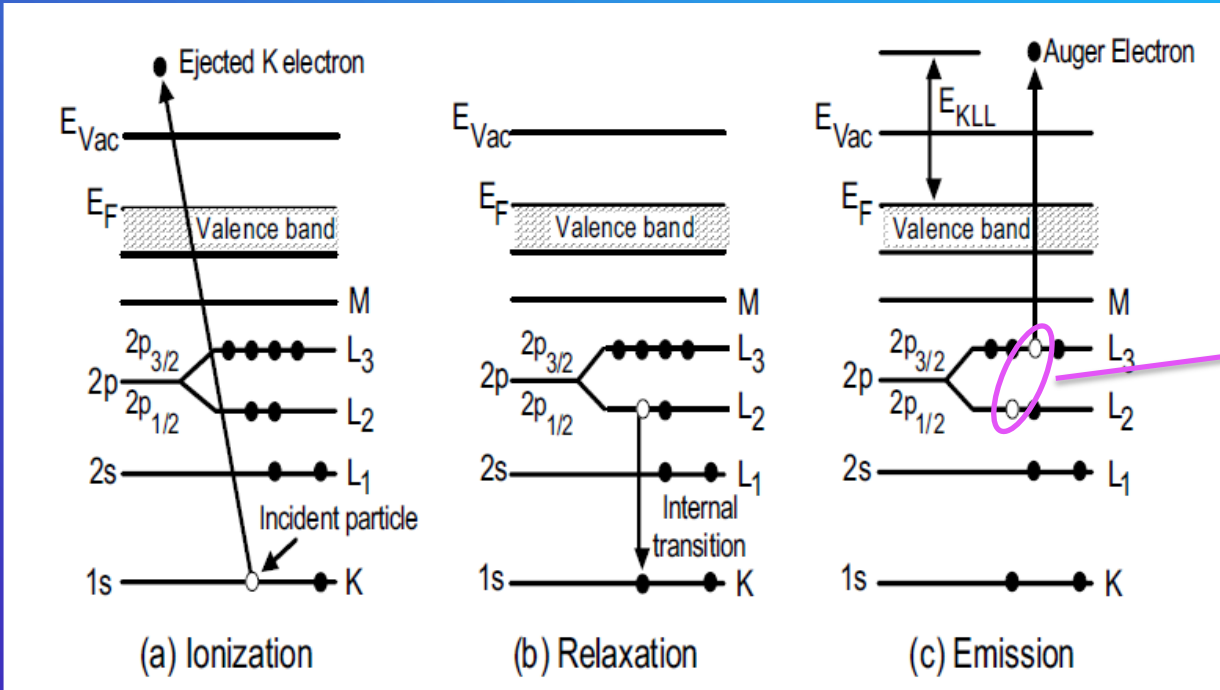


SAM by MacDonald
and Waldrop, 1971



Paul Palmberg,
1972

Principles



ionized twice

Naming



X = An Optional Element

$\hbar\vartheta$ = Energy of Primary Beam

Core State = The letter of the shell, on which the vacancy was formed

B = The letter of the shell, from which the electrons filled this vacancy

C = The letter of the shell, from which the third electron (Auger electron) was emitted

Final Electron Configuration	Auger Transition
$2s^0 2p^6$	KL ₁ L ₁
$2s^1 2p^5$	KL ₁ L ₂ KL ₁ L ₃
$2s^2 2p^4$	KL ₂ L ₂ KL ₂ L ₃ KL ₃ L ₃

Kinetic Energy

- $E_{Kin} \approx E_{Core\ State} - E_B - E_C - E_{Atomic\ Bondings} - E_{Loss\ @\ Analyzer}$

$$E_C^*$$

$$\approx 4\ eV$$

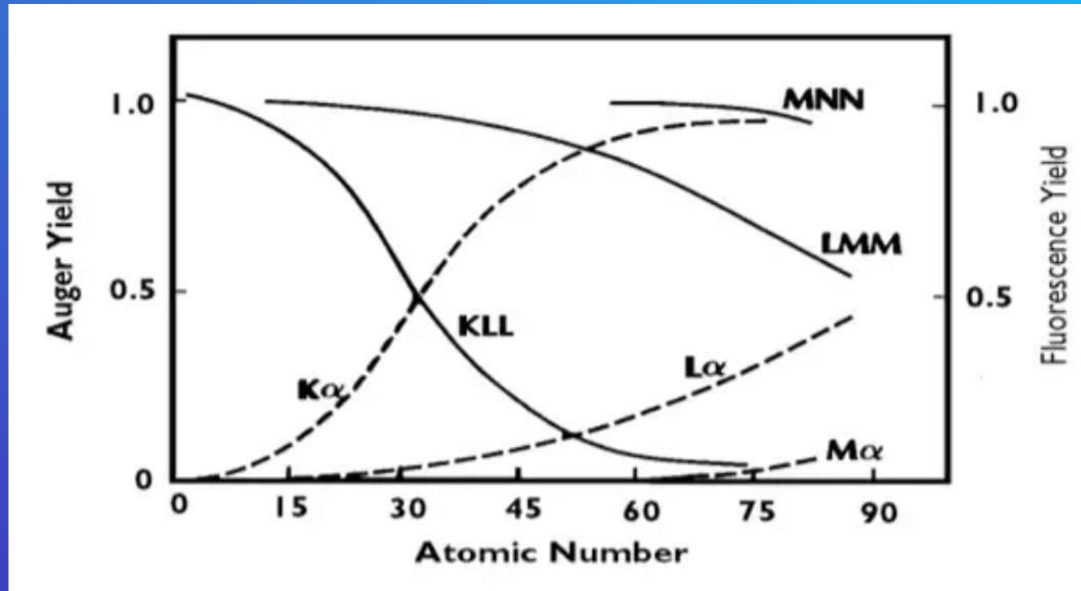
depends on Fermi Levels

$E_{KL_1L_3}$ Transition @ Aluminium :

$$\begin{aligned} E_{KL_1L_3} &\approx E_K - E_{L_1} - E_{L_3} \\ &\approx 1560 - 118 - 73 \\ &\approx 1369\ eV. \end{aligned}$$

Experimentally Measured 1354 eV $\rightarrow E_{Atomic\ Bondings} + E_{Loss\ @\ Analyzer} \approx 1369 - 1354 = 15\ eV$

Fluorescence Yield vs. Auger Yield



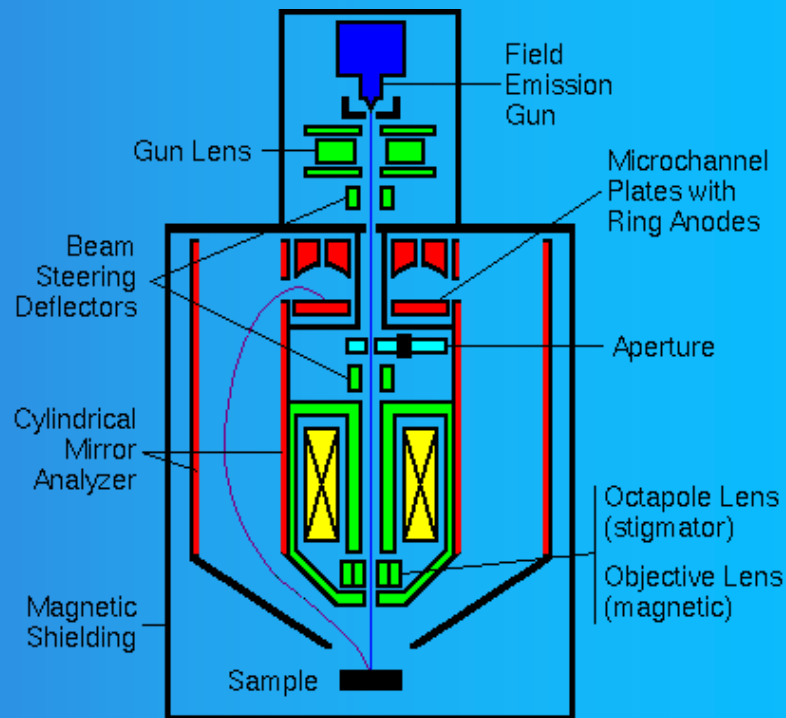
Probability of X – ray Emission $\approx 1 -$ Probability of Auger Electron Emission

Instrumentation

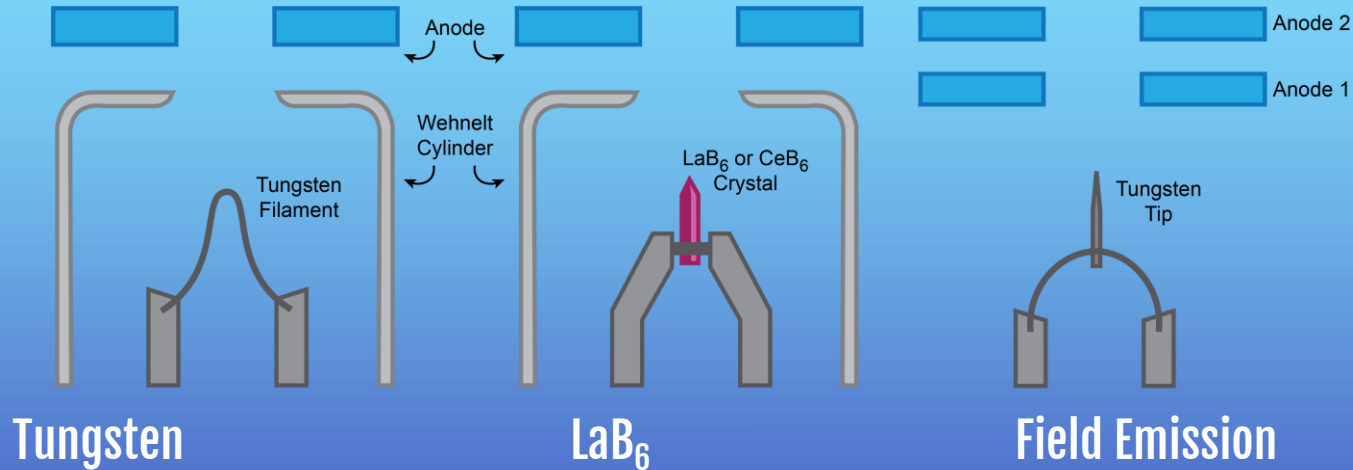
- **Electron Guns:** produces electron beam
- **Electron Optics:** a set of electron optics is used to deliver electrons
- **Analyzer:** a chamber which is responsible for the delivery of auger electron to detector
- **Detector:** provides multichannel detection of the number of electrons and their energy
- **Sample Stage**
- **UHV Chamber:** ultra high vacuum chamber (Pressure= 10^{-9} torr)
- **Ion Gun:** depth profile measurement
- **Secondary Electron Detector:** SAM mapping and imaging
- And...

Instrumentation

Modern instruments nearly always incorporate cylindrical mirror analyzers because their high transmission efficiency leads to better signal-to-noise ratios. The schematic shows a cross section of a cylindrical mirror analyzer in red. The primary electron beam hits the sample surface at the source point of the analyzer. Auger electrons move outward in all directions and some pass through the grid covered aperture in the inner cylinder. A variable negative potential on the outer cylinder bends the Auger electrons back through a second aperture on the inner cylinder and then through an exit aperture on the analyzer axis. The energy of transmitted electrons is proportional to the voltage ($-V$) on the outer cylinder.



Electron Gun



A Tungsten wire filament bent in the shape of a hairpin

Lanthanum hexaboride (LaB₆) cathodes provide higher current densities because LaB₆ has greater emissivity than tungsten

Field Emission electron sources consist of very sharp tungsten points at which electrical fields can be $>10^7$ V/cm. At these fields, electrons tunnel directly through the barrier.

Electron Spectrometers

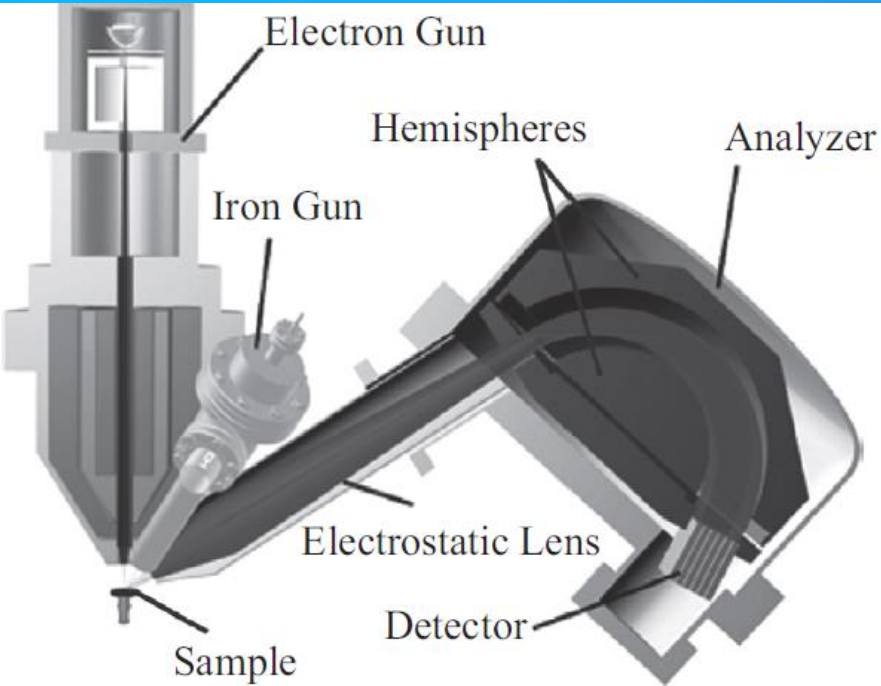
A spectrometer consists of an electron energy analyzer with an electron detector at its output. All practical electron energy analyzer concepts are based on retardation or deflection of electrons as they pass through an electric or magnetic field, the degree of retardation/deflection being in some manner proportional to their energy or velocity. Two mostly used analyzers are:

Cylindrical Mirror Analyzer (CMA)

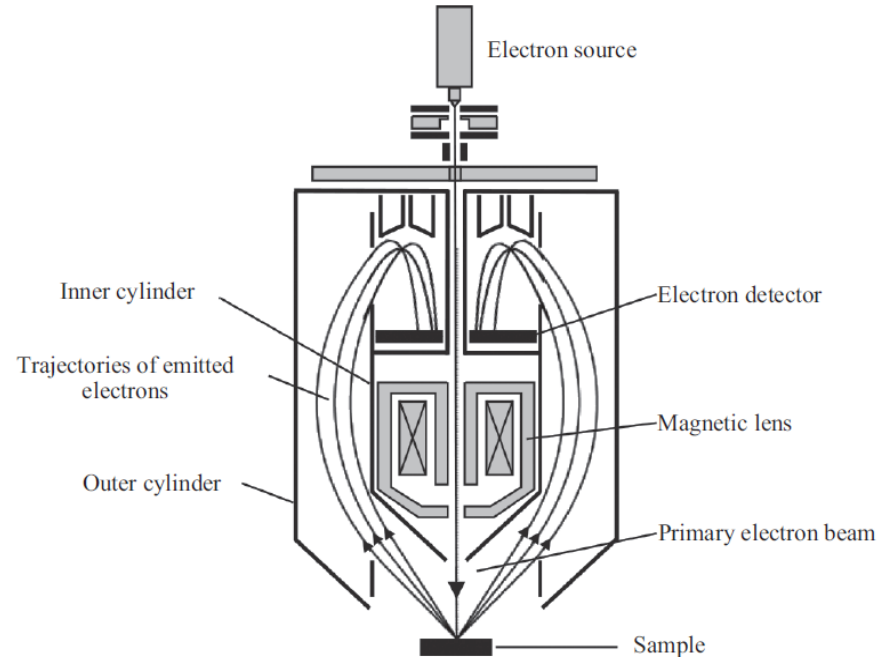
Concentric Hemispherical Analyzer (CHA).

ANALYZERS

HSA

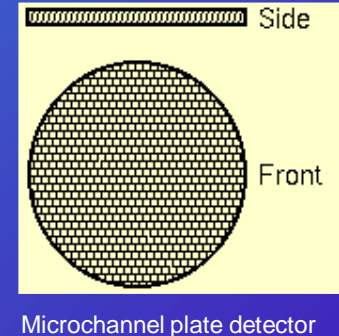
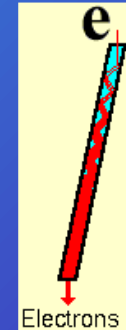
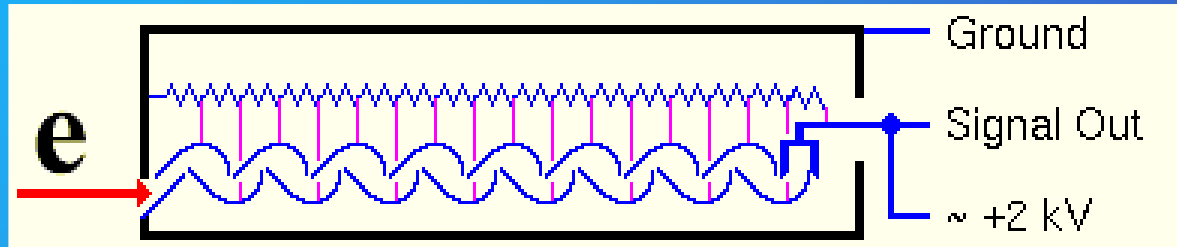


CMA



Electron Detector

An electron multiplier consists of a series of electrodes called dynodes connected along a resistor string. The output end of the resistor string is attached to a positive high voltage. The other end of the string goes to the electron multiplier case and ground. The dynode potentials differ in equal steps along the chain. When a particle (electron, ion, high energy neutral, or high energy photon) strikes the first dynode, it produces secondary electrons. The secondary electrons are accelerated into the next dynode where more secondary electrons are produced. A cascade of secondary electrons ensues. The dynode acceleration potential controls the electron gain



Samples



Forms

Solid with low vapor pressure



Size

Limited by the sample stage, 2*1*1 cm is typical



Topography

Flat surfaces are preferable; rough surfaces may be analyzed either in small areas or averaged over large areas



Preparation

Frequently none; samples must be free of fingerprints, oils, and other high-vapor-pressure materials

Application

- Qualitative and quantitative surface analysis
- **Distribution of chemical species:** AES can detect almost all elements except H and He and also is used for extraction of composition of some surface components
- **This film studies:** detection of surface elements up to 2nm
- Grain boundary segregation, corrosion, insulating samples and mineralogy studies
- Depth profile measurement: using Ar gun to study depth, layer by layer
- Scanning Auger Microscope

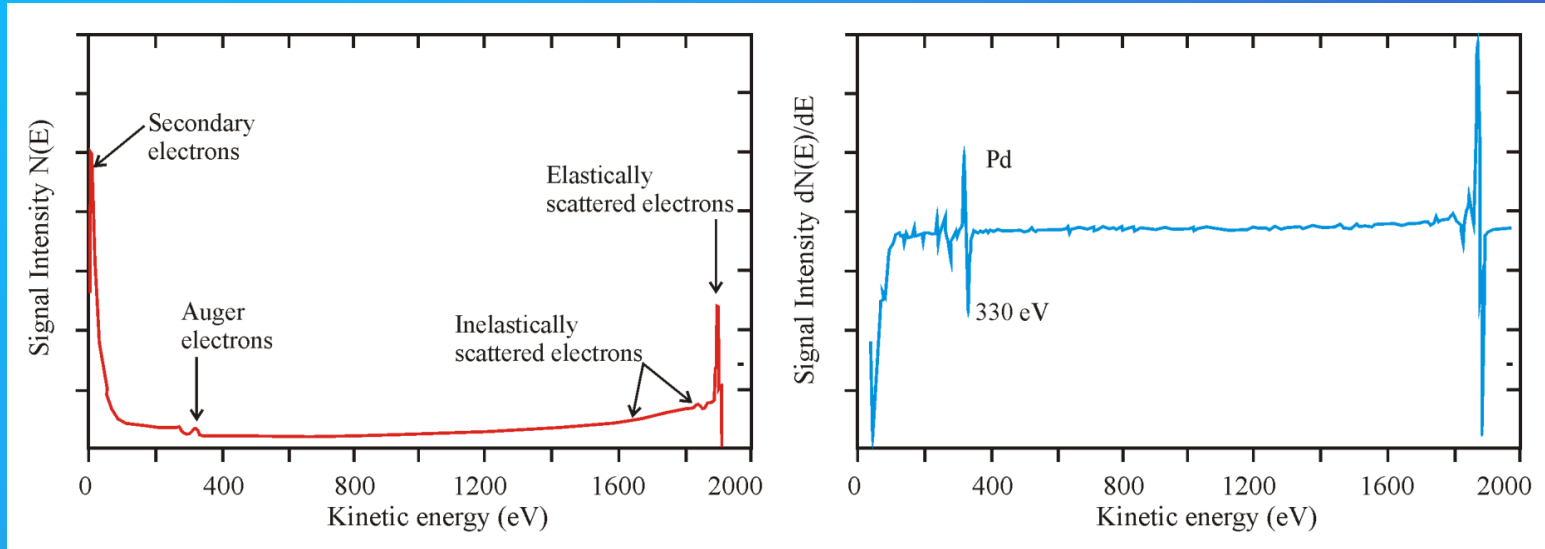
AES vs.



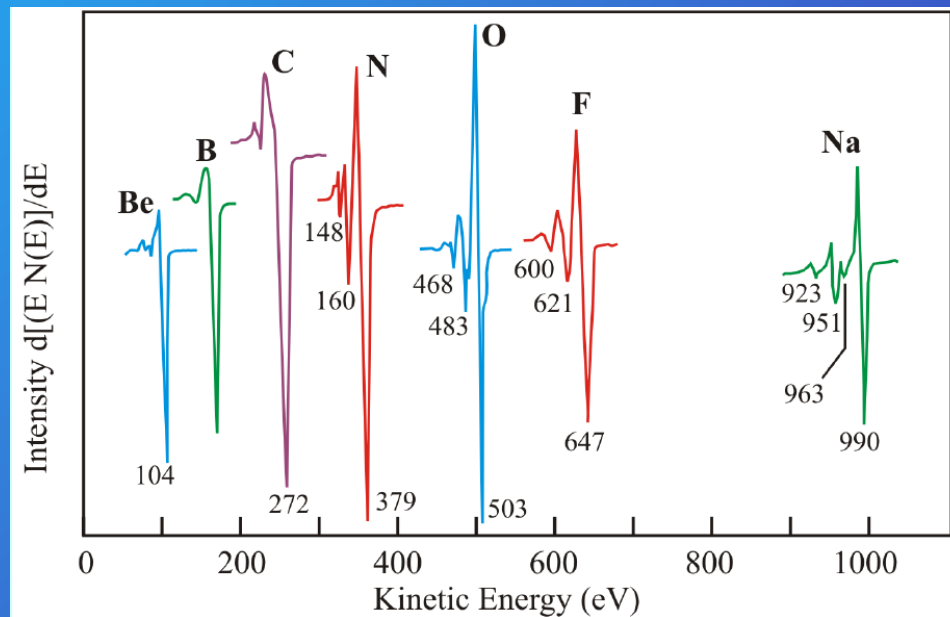
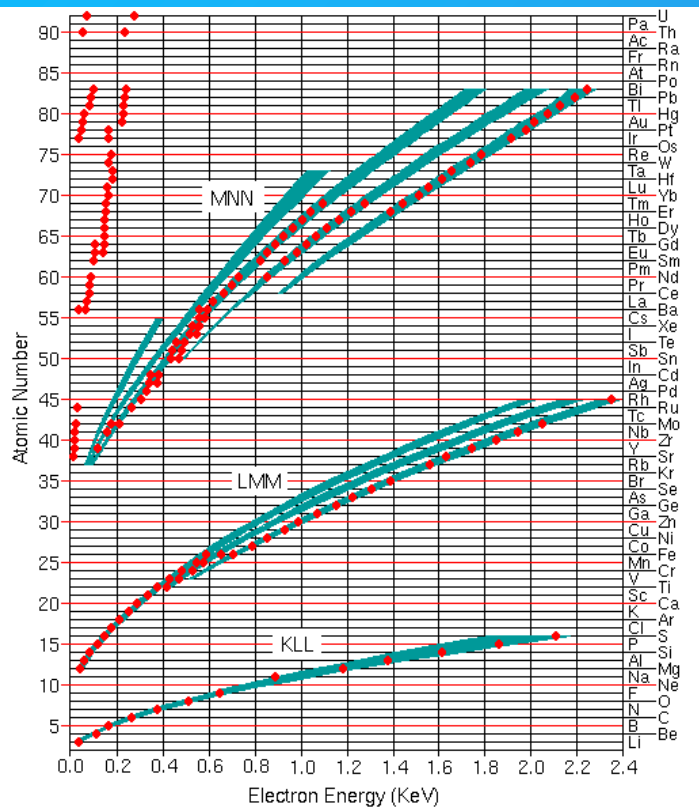
AES vs. XRF

X-Ray Fluorescence Spectroscopy	Auger Electron Spectroscopy
Applications	
<ul style="list-style-type: none"> • Detection and quantification of elements with atomic number 5 or higher. • Detection limits for bulk determinations are normally a few parts per million (ppm) to a few tens of ppm, depending on the x-ray energy used and the sample matrix composition. • For thin-film samples, detection limits are approximately 100 ng/cm². 	<ul style="list-style-type: none"> • Analysis of surface contamination of materials to investigate its role in properties such as adhesion, wear, corrosion, secondary electron emission, and catalysis • Identification of chemical-reaction products, for example, in oxidation and corrosion • In-depth compositional evaluation of surface films, coatings, and thin films used for various metallurgical surface modifications and microelectronics applications • Evaluation of surface and buried defects in microelectronics • Analysis of grain-boundary chemistry to evaluate the role of precipitation and impurity segregation on mechanical properties, corrosion, and stress-corrosion cracking • Can detect all elements except hydrogen and helium
X-Ray Fluorescence Spectroscopy	Auger Electron Spectroscopy
General Use	
<ul style="list-style-type: none"> • Qualitative and quantitative chemical analysis for major and minor elements in metals and alloys. • Determination of composition and thickness of thin-film deposits. 	<ul style="list-style-type: none"> • Compositional analysis of the 0.5 to 5 nm region near the surface for all elements except hydrogen and helium. • Chemical-state analysis is possible in selected cases. • Depth-compositional profiling and thin-film analysis • High lateral-resolution surface analysis in areas > 20 nm
Samples	
<ul style="list-style-type: none"> • Samples may be bulk solids, powders, pressed pellets, glasses, fused disks, or liquids. • Bulk metal samples typically are ground to produce a flat, uncontaminated surface for analysis. Typical samples have dimensions of several centimeters; however, most instruments can accommodate samples 10 cm (4.0 in.) or more in diameter. • Powder samples are typically attached to a non-x-ray-producing substrate or are pressed into pellets. • The technique is completely nondestructive. • Sampling depth may range from a few micrometers to a millimeter or more, depending on the x-ray energy used and the matrix composition of the sample. 	<ul style="list-style-type: none"> • Form: Solids (metals, ceramics, and organic materials with relatively low vapor pressures). High-vapor-pressure materials can be handled by sample cooling. Many liquid samples can be handled by sample cooling or by applying the sample as a thin film onto a conductive substrate. • Size: Individual powder particles as small as 20 nm in diameter can be analyzed. Maximum sample size depends on the instrument; typical is 6 cm (2.4 in.) in diameter by 1.5 cm (0.6 in.) in height. • Surface topography: Flat surfaces are preferable, but rough surfaces such as fracture surfaces can be analyzed. • Preparation: Frequently not necessary. Samples must be free of fingerprints, oils, and other high-vapor-pressure materials.

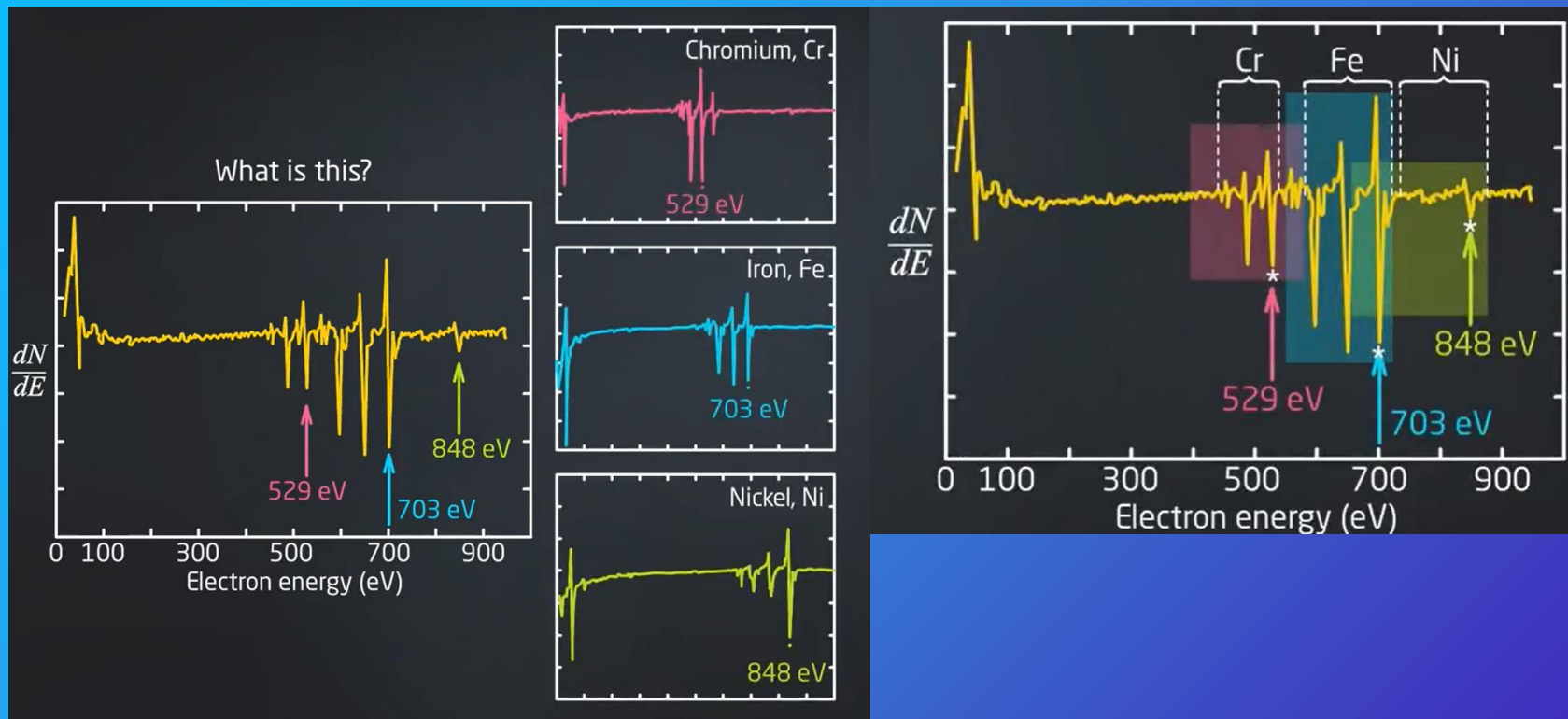
Data interpretation



Data interpretation



Data interpretation



Quantitative Analysis

- If we assume a homogeneous sample, $N_i = \text{atoms/cm}^3$, $A_i = \text{detector count rate}$, concentration to be a ratio of atoms, $\chi_i = \text{auger transition probability}$, $r = \text{secondary ionization coeff}$, $\lambda_i = \text{inelastic electron mean free path}$ and $\sigma_i = \text{ionization(scattering) cross-section}$ and T as the analyzer transmission function, we may write:

- $$N_i = A_i / \sigma_i \chi_i (1+r) T(E_i) \lambda_i(E_i)$$

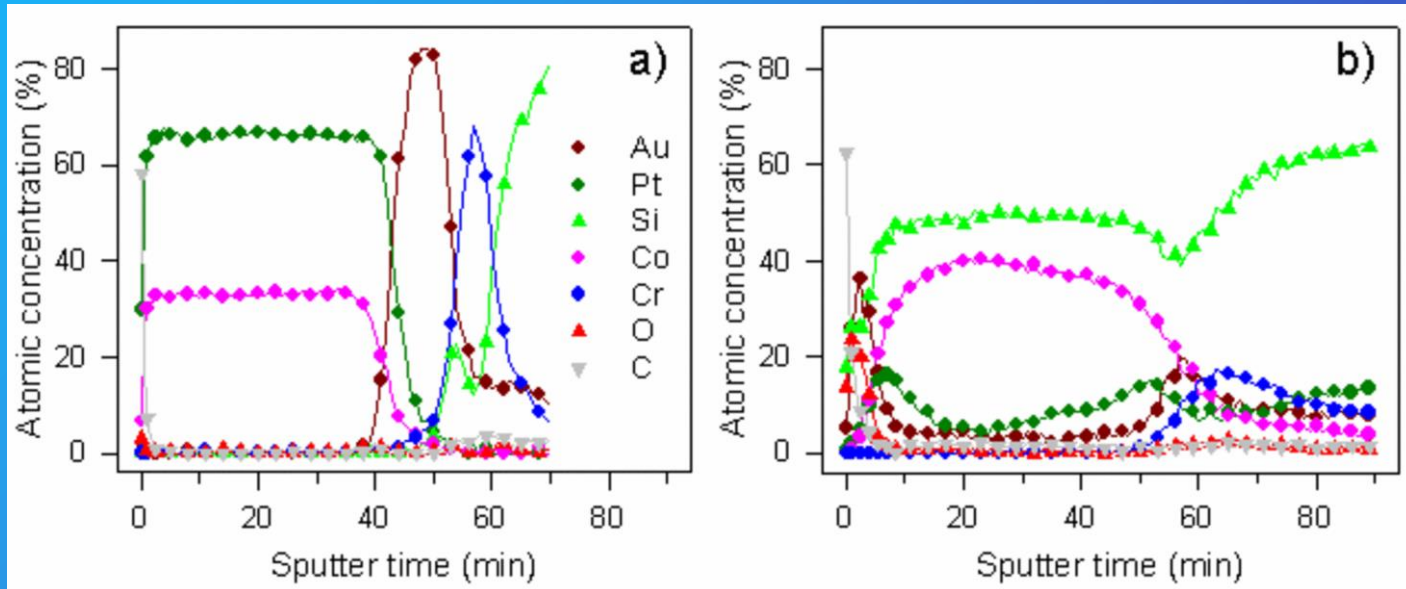
It is difficult to determine λ_i and r , so they are usually neglected. Modern software uses the equation below:

- $$C_i = (A_i/S_i) / (\sum A_{i,j}/S_{i,j})$$

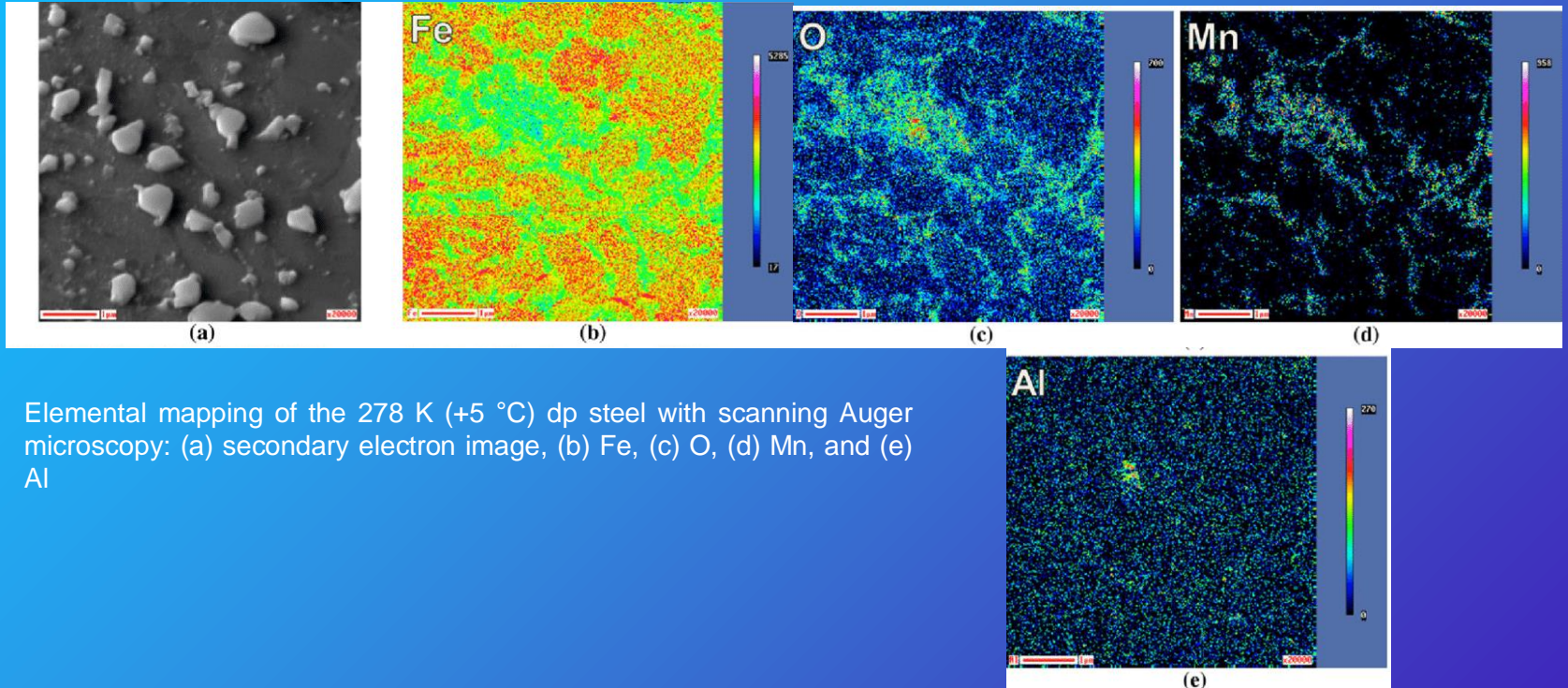
C_i is the concentration of element i and S_i are sensitivity factors and are determined with standards.

Depth profiling

The presence of an ion gun on an AES instrument allows the analyst to make depth profile measurements, measuring elemental concentrations as a function of depth. In an AES instrument, depth profiling is almost exclusively conducted using argon ions. Pictures show Co-Pt films before and after annealing



Imaging, using auger electron



Elemental mapping of the 278 K (+5 °C) dp steel with scanning Auger microscopy: (a) secondary electron image, (b) Fe, (c) O, (d) Mn, and (e) Al

Summary

- **Elements:** Li and above
- **Limit of detection:** 0.1-1 atomic percent
- **Chemical composition:** quite hard, but chemical comp. is available for some components
- **Sample type:** UHV-compatible
- **Lateral Resolution:** 500nm
- **Depth resolution:** 0.5-5nm
- **Depth profile measurement:** using Argon gun to study depth, layer by layer

RESOURCES

- E. Wyroba, S. Suski, K. Miller, R. Bartosiewicz, "Biomedical and agricultural applications of energy dispersive X-ray spectroscopy in electron microscopy", Cellular and Molecular Biology Letters, 2015.
- <https://en.wikipedia.org/wiki/Cathodoluminescence>
- https://en.wikipedia.org/wiki/Auger_electron_spectroscopy
- <http://www.xpsfitting.com/2009/03/auger-process-and-notation.html>
- <https://www.coursera.org/lecture/methods-surface-analysis/auger-spectroscopy-operating-principles-facility-scheme-LHR4s>
- Richard P. Gunawardane and Christopher R. Arumainayagam, "Handbook of Applied Solid State Spectroscopy", Chapter 10 (Auger Electron Spectroscopy), Springer, Boston, MA, 2006.
- Auger Electron Spectroscopy(AES), Prof. Paul K. Chu
- K. Žužek Rožman et al.; J. Magnet. Magnet. Mat. 314 [2] (2007) 116-121.
- Methods of Surface Analysis by National Research Nuclear University MEPhI