EPFL

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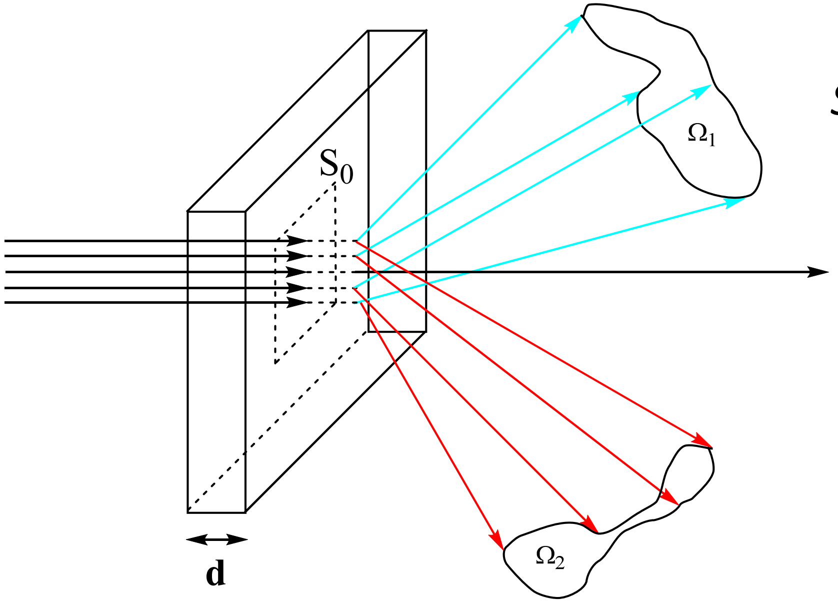
Physical and Chemical Analyses of Materials

Chemical analysis: AES

Introduction

⇨ The principal beam-matter interactions with matter are depicted below:



$\overrightarrow{\mathbf{k}_0}, \mathbf{I}_0, \mathbf{E}_0$

Primary beam

$\overrightarrow{\mathbf{k}_1}, \mathbf{I}_1, \mathbf{E}_1$

Strongly modified primary beam

scattering

$\overrightarrow{\mathbf{k}_0}, \mathbf{I}_0', \mathbf{E}_0$

Slightly modified primary beam

absorption

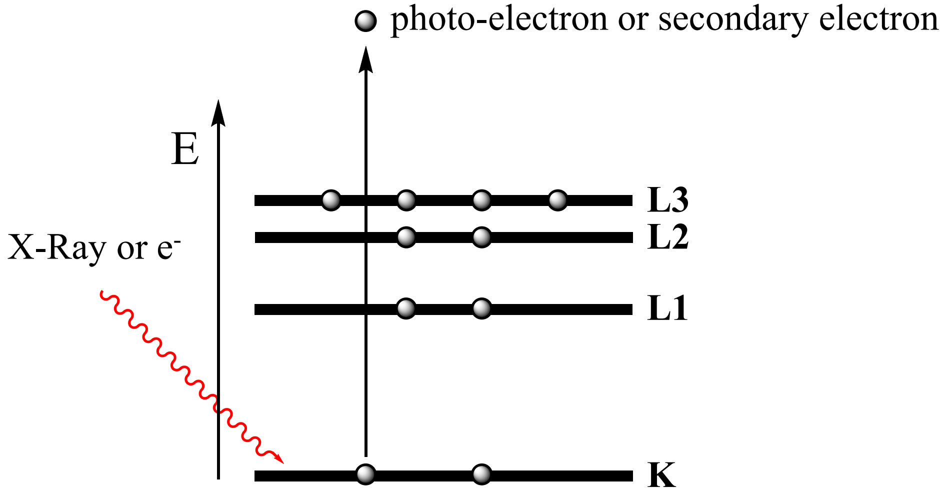
$\overrightarrow{\mathbf{k}_2}, \mathbf{I}_2, \mathbf{E}_2$

Secondary beam

emission

⇨ In material analysis, the use of X-Rays and electrons as exciting beams generally causes the ionisation of the matter.

- The inelastic interactions between a beam and core electrons can be described at the atomic level as:



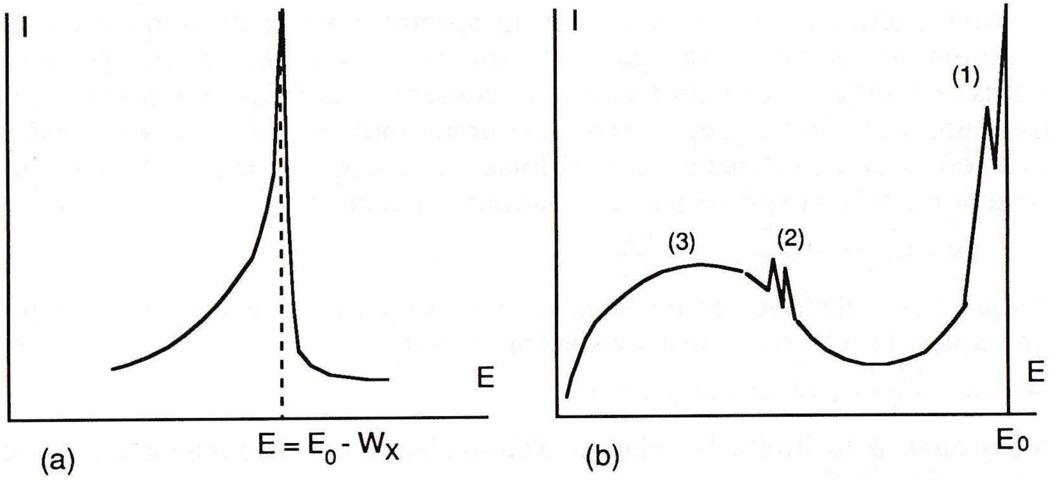
  - According to the energy of the primary beam, the interactions core electron-beam generally lead to the ionisation of the target atom.
  - For X-Rays primary beams, the ejected electron is called a photo-electron.
  - For electrons primary beams, the ejected electron is called a secondary electron (SE).

- The life time of such an ionised state is about 10^{-16} s. Afterwards, the matter relaxes. The matter relaxation can lead to either X-Rays or to an Auger electrons emission.

⇨ Secondary electrons are produced with a widespread energy because the energy loss by the primary electrons is not quantified.

↬ Before being able to leave the material, they undergo many elastic and inelastic interactions with the surrounding matter. Secondary electrons reach the surface when emitted from a superficial layer of thickness lower than their free mean path **l**.

↬ In contrast with photo-electrons, one can not precisely correlate the kinetic energy of these secondary electrons to the chemical nature of their emitting elements. There are not used for chemical analysis.

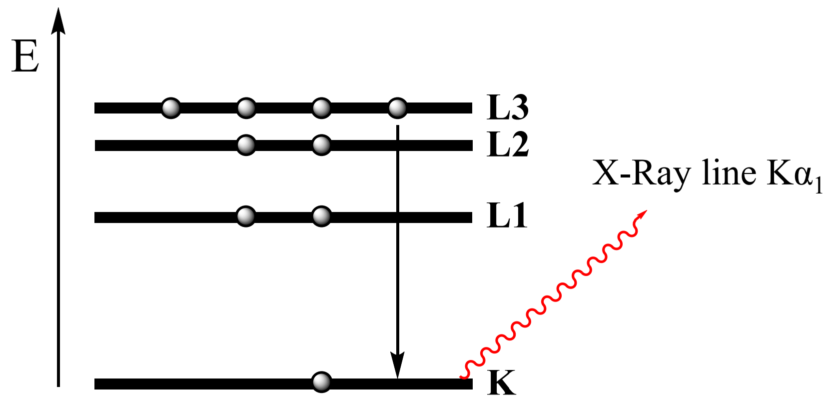


↬ After several interactions, the primary electrons loose energy and so increase their probability to be involved in elastic scattering events.

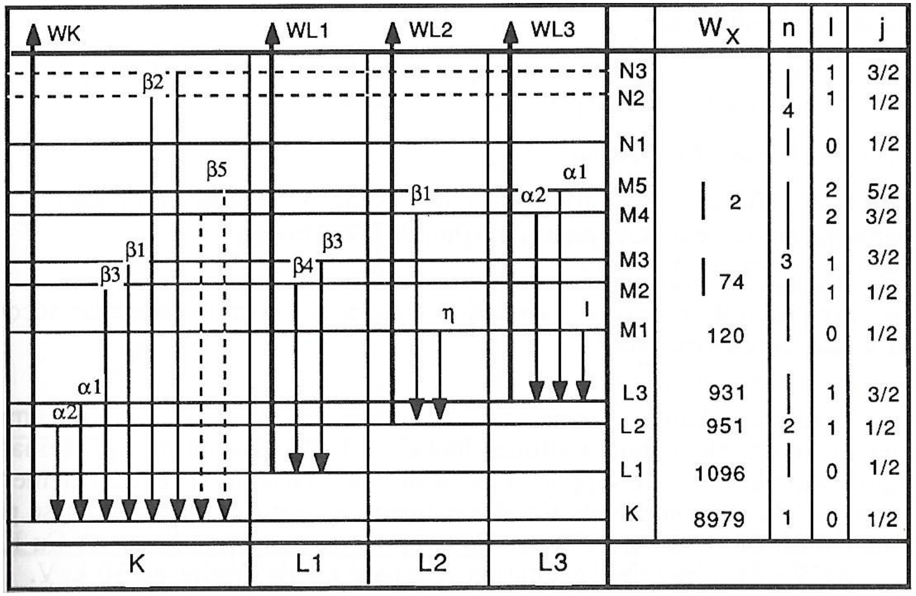
Emission electron spectra (intensity as a function of the energy) for photo-electrons from X-rays excitation (**a**) and secondary electrons from primary electrons excitation (**b**). 1: elastic scattering and plasmons, 2: Auger electrons, 3: secondary electrons.

Ionised matter relaxation by X-Rays emission

⇨ The matter relaxation can lead to the emission of an X-Ray photon:



electronic transitions are allowed for: $|\Delta n| \geq 1; \Delta l = \pm 1$; $\Delta j = 0, \pm 1$.

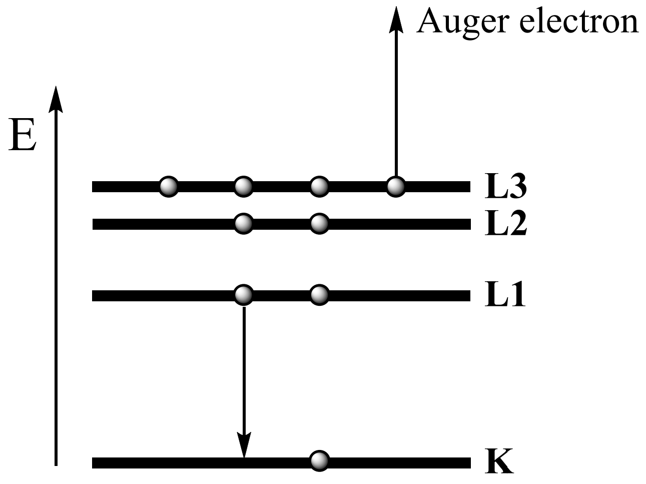


⇘ Above is gathered the emission lines for copper. W_x relates to the ionisation energies for a level **X**. The notation Kα1; Kβ… relates to the Siegbahn notation. For a transition **KL3** the emission line is called $K\alpha_1$.

⇘ The excitation of the matter being localised at an atomic deep level, the X-Ray lines are not affected by the chemical bonds.

Ionised matter relaxation by Auger electrons emission

⇨ The energy emitted by the relaxation of an ionised atom can be used to eject an Auger electron:



↳ The energy associated to the transition **L1 → K** is communicated to an electron **L3**.

↳ As the ionisation energy of this electron is lower than the transition energy **KL1**, this electron is ejected with a noticeable kinetic energy.

↳ The Auger transition is called **KL1L3**.

Final Electron Configuration	Auger Transition
$2s^0 2p^6$	$KL_1 L_1$
$2s^1 2p^5$	$KL_1 L_2$ $KL_1 L_3$
$2s^2 2p^4$	$KL_2 L_2$ $KL_2 L_3$ $KL_3 L_3$

⇨ For a transition **XYY'**, the kinetic energy of the Auger electron depends on the energy of the **XY** transition and on the ionisation energy of the Auger electron **Y'**.

↳ For a **XYY'** transition, when the Auger electron does not undergo any interaction with the surrounding matter, its characteristic energy for an element of atomic number **Z** is:

$$\mathbf{Ec_0(Z) = W_X(Z) - W_Y(Z) - W_{Y'}(Z+1)}$$

↳ $\mathbf{W_{Y'}(Z+1)}$ is introduced for tacking into account that the Auger electron is ejected from an ionised atom.

↳ As for the photo-electron, to leave the material, the Auger electron must also counteract the potential barrier **Φ** of the surface corresponding to an extraction energy **eΦ**. If no interaction occurs between the Auger electron and the surrounding matter, its kinetic energy will be:

$$\mathbf{Ec = W_X(Z) - W_Y(Z) - W_{Y'}(Z+1) - e\Phi}$$

↳ After ejection, the Auger electron must migrate from the bulk material to its surface. During this travelling, it can bump other electrons through elastic and inelastic interactions with the surrounding matter. In this case, the detected Auger electron will have a kinetic energy lower than **Ec**.

⇨ The selection rules for the Auger electron emission are the following:

↳ A transition **XYY'** is allowed if $\mathbf{W_{Y'} < W_X - W_Y}$: $\mathbf{Ec_0 > 0}$.

↳ Some Auger transition with $\Delta \mathbf{n} = \mathbf{0}$ are allowed like **L1L2M1** or **L1L3M1** for example. These transitions are named Koster – Kronig transitions.

↳ For particular atoms, the $\mathbf{Ec_0 > 0}$ condition can not be satisfied. So some transitions like **L1L3M5** are forbidden for atoms with an atomic number **Z** included in the range: $\mathbf{40 < Z < 73}$.

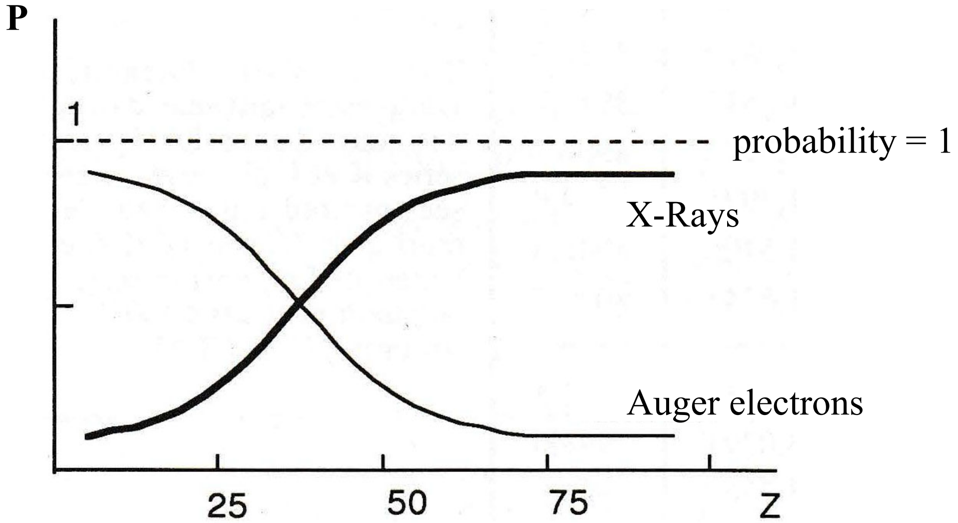
↳ Experimental data showed that Auger transitions caused by the primary ionisation of **s** electrons are favoured.

↳ The number of possible **XYY'** transitions increases a lot with the atomic number of an element that complicates the Auger spectra and so their interpretations. Below is given a short list of possible Auger transitions: **KL1L1**, **KL1L2**, **KL1L3**, **KL2L2**, **KL2L3**, **KL3L3**, **KL1M1**,…, **L1M1M1**,…

Competition between Auger electrons and X-Rays emission

⇨ The Auger electrons and X-Rays emissions are in competition, depending on the atomic number of the emitting element.

⇨ The intensities of the Auger transitions are complementary to the X-Ray transition ones and depend on the atomic number of the considered element:



$$\mathbf{I}_{\mathbf{Auger}} = \mathbf{v}\frac{\mathbf{P}_{\mathbf{Auger}}}{\mathbf{P}_{\mathbf{Auger}} + \mathbf{P}_{\mathbf{X-Ray}}}$$

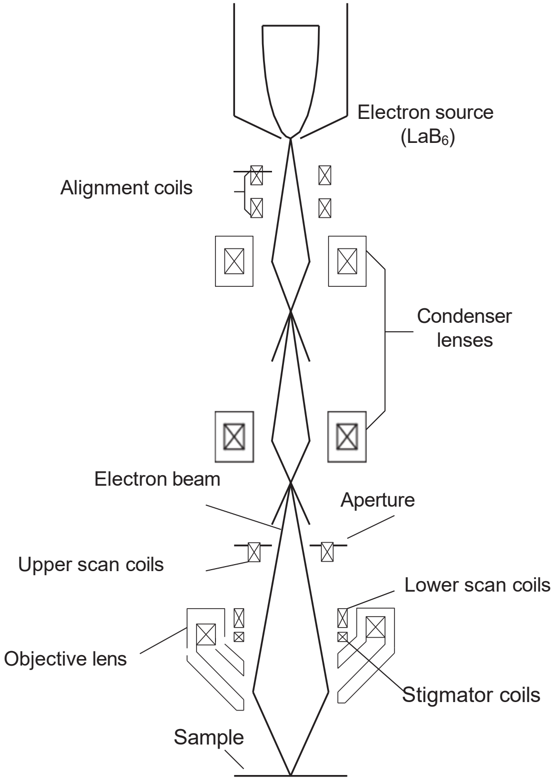
⇨ **v** is the rate of ionisation of the primary energy level, $\mathbf{P}_{\mathbf{Auger}}$ and $\mathbf{P}_{\mathbf{X-Ray}}$ are related to the probabilities of these emissions.

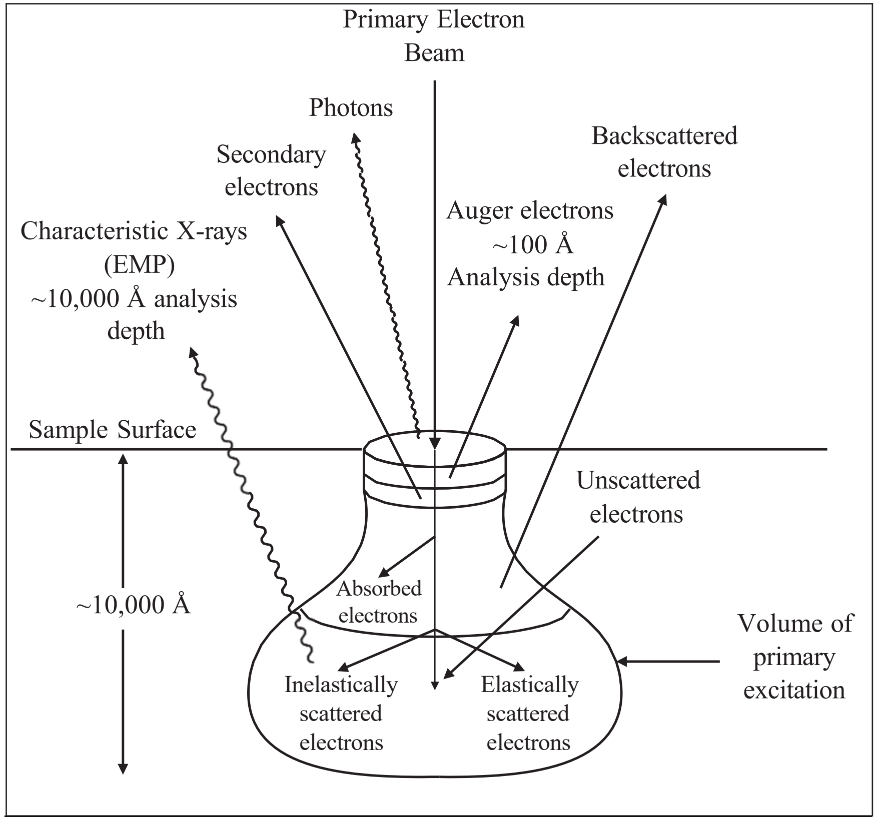
⇨ The Auger effect disturbs the X-Ray emissions: modification of the relative intensity of the lines of different series, displacement of the energy levels which causes the appearance of satellites lines.

⇨ The presence of Auger transitions broadens the X-Ray lines, especially for light elements.

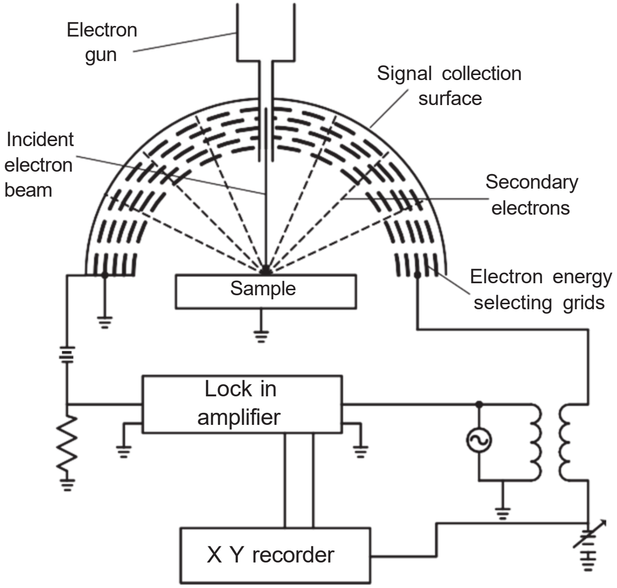
⇨ The chemical shift for Auger transitions is more important that for X-Ray transitions. It is more pronounced for light elements and for transitions in which valence band electrons are involved.

Electron source and electron-sample interaction

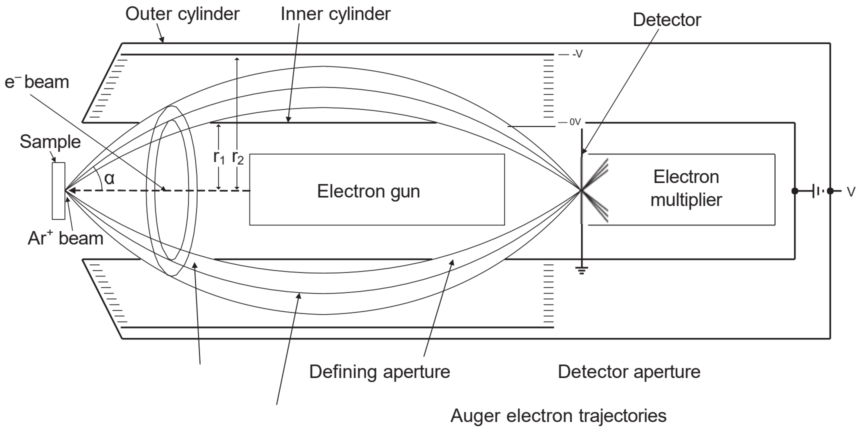




Spectrometers

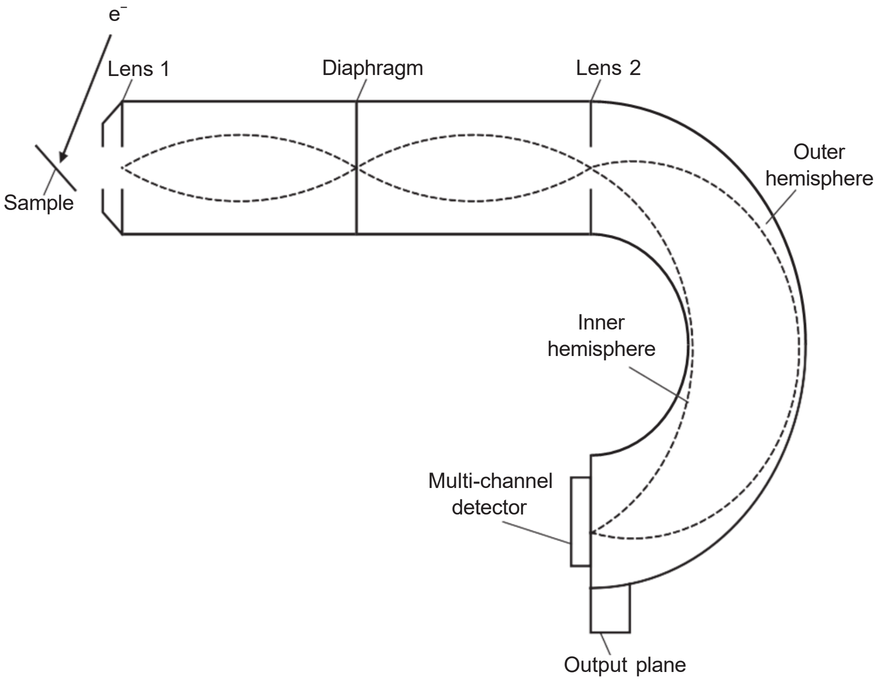


A schematic diagram of the retarding field analyzer

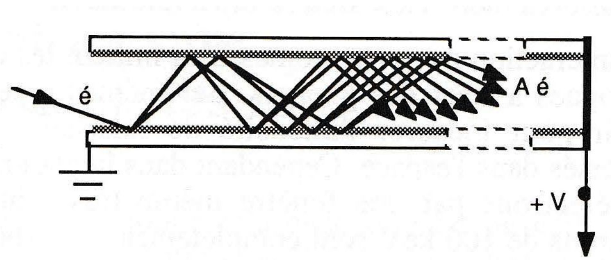


A schematic diagram of the cylindrical mirror analyzer

Chemical analysis: AES



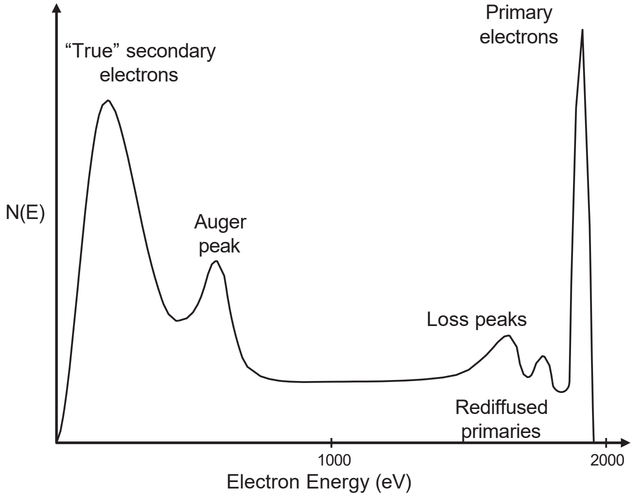
A schematic diagram of the concentric hemispherical analyzer



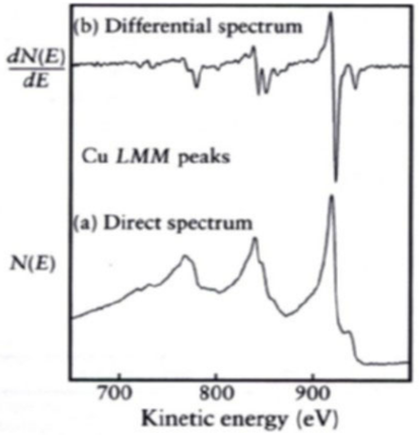
⇨ A channetron detector is the most common detector in AES instruments.

↳ In this scheme, **A** stands for the amplification coefficient.

AES spectrum



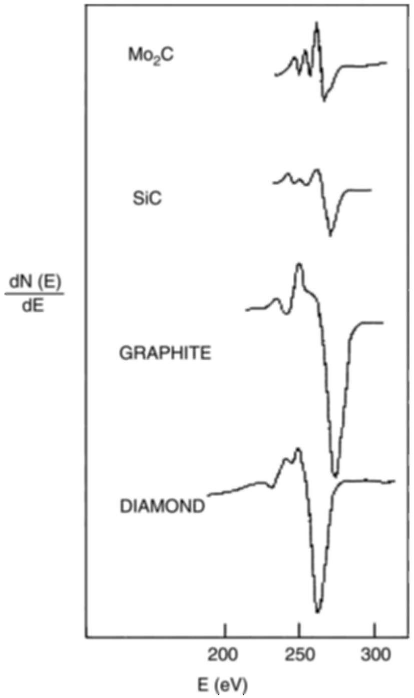
Schematic diagram of the energy distribution of secondary and backscattered electrons produced by the interaction of a nearly monochromatic electron beam with a solid



The direct and differentiated spectrum of copper

⇨ The Auger transitions of choice for the different elements can be summarized as follows: $3 < Z < 14$ (KLL transitions), $14 < Z < 40$ (LMM transitions), $40 < Z < 82$ (MNN transitions), and $82 < Z$ (NOO transitions).

Chemical analysis: AES



Effect of chemical environment on the KLL Auger spectra of carbon. The shift in the Auger peak energy for diamond is due to charging of the insulator.

Chemical analysis: AES

AES depth profile analysis of tin plated can: