

Physical and Chemical Analyses of Materials

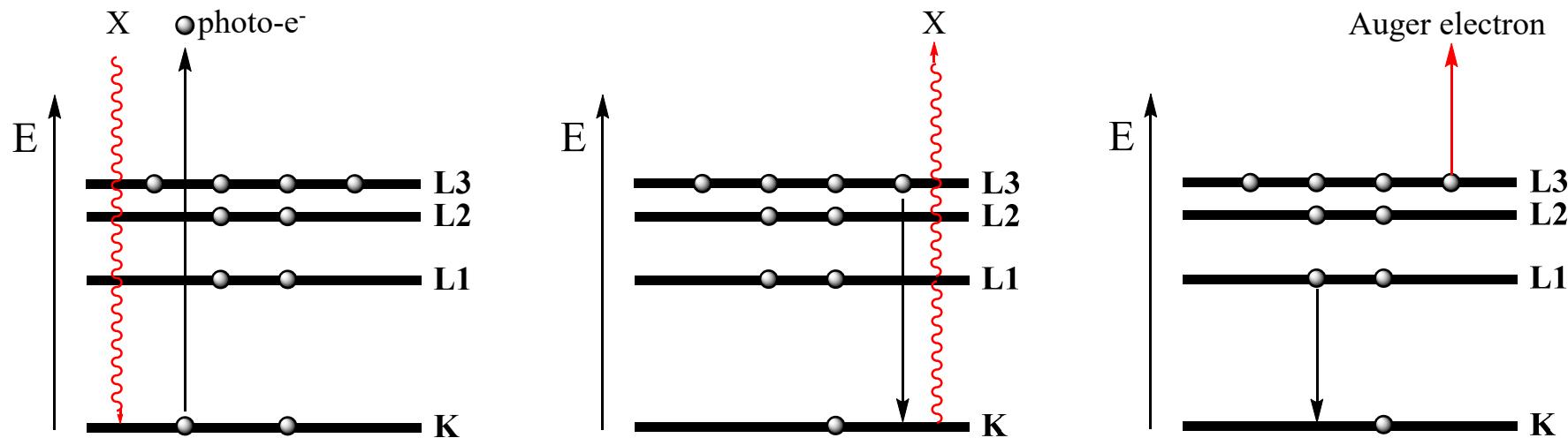
Chemical analysis: X-Ray Photoelectron Spectrometry

Introduction

- ⇒ X-Ray Photoelectron Spectrometry refers to the analysis of the electrons emitted by the matter when excited by a primary X-Ray beam. This method was developed by Kai Siegbahn during the 50's which was awarded by the Nobel Price of Physics in 1981.
- ⇒ It is a qualitative and a quantitative elementary surface analysis of materials called XPS or sometimes ESCA (Electron Spectroscopy for Chemical Analyses).
- ⇒ XPS is a chemical analysis which is not coupled to any microscopic device as it is the case for XRMA.
- ⇒ Nevertheless XPS can provide 2D-maps corresponding to the chemical composition of the surface of a given material but suffers from a weak lateral resolution about 10 μm due to the primary beam size (see after).
- ⇒ The analysed photoelectrons are emitted from 10 nm depth of the material at the maximum that places XPS as a analytical method dedicated to surface studies.
- ⇒ XPS shares with XRFS a few devices like the X-Ray tube and the beam optics. The difference between and XPS and XRFS is mainly related to the detection system which is dedicated to the analysis of surface electrons in the case of XPS and X-Ray photons in the case of XRFS.

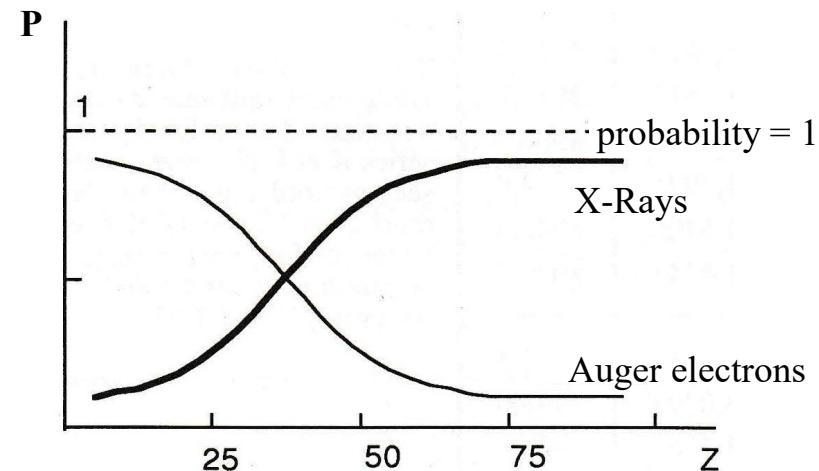
Interaction X-Ray-Matter

⇒ The interaction between the X-Rays and the matter is depicted below:



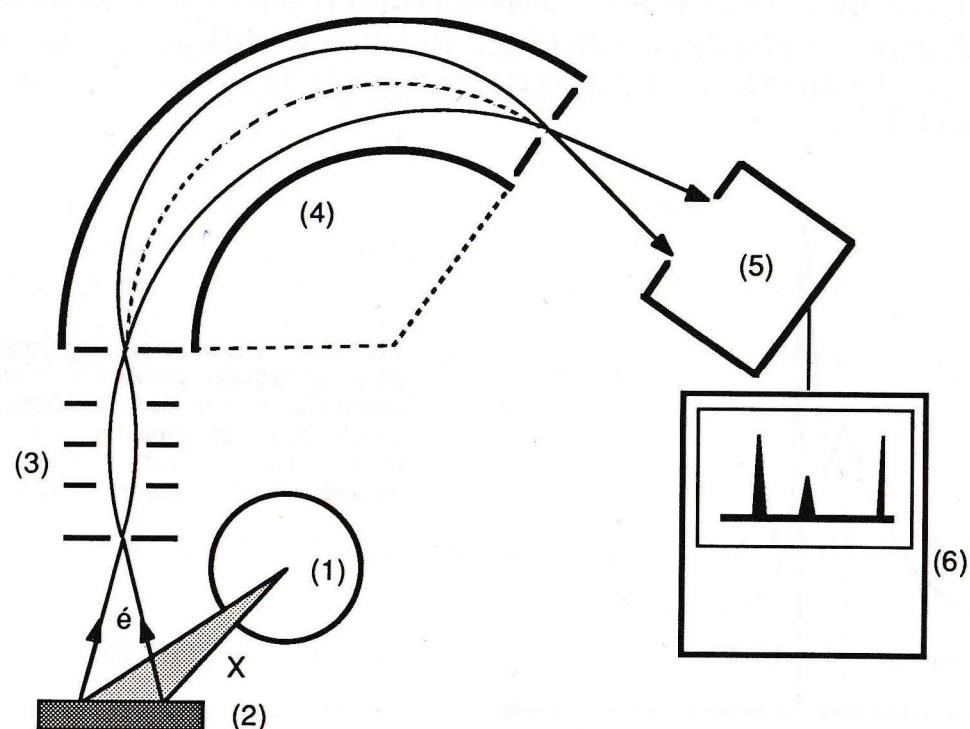
⇒ In contrast with XRFS, XPS does not suffer from interferences caused by the nature of the primary beam.

⇒ Only Auger electrons will be clearly visible on an XPS spectrum, especially when analysing light elements.



XPS instrument

⇒ The scheme of an XPS instrument is presented below:

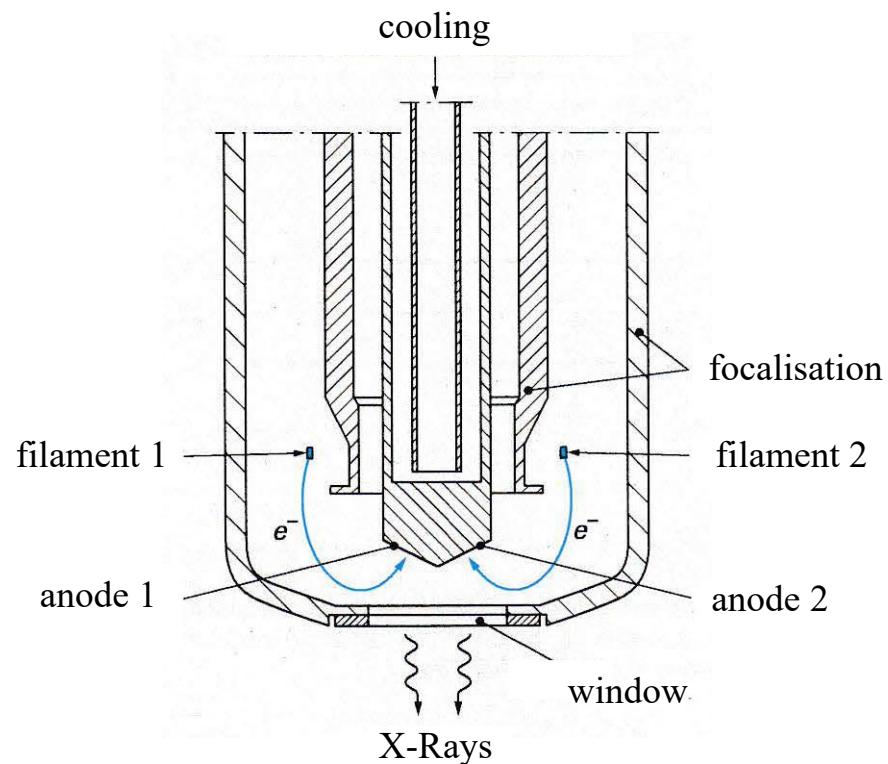


X-Ray tube equipped with a monochromator (1), sample (2), electron focusing system (3), concentric hemispherical analyser (4), electron detector (5), acquisition system (6).

⇒ As the principle of an XPS instrument is based on the signal given by electrons, it requires an ultrahigh vacuum. The sample chamber is at 10^{-12} Bar and the spectrometer is at 10^{-9} Bar.

X-Ray tube

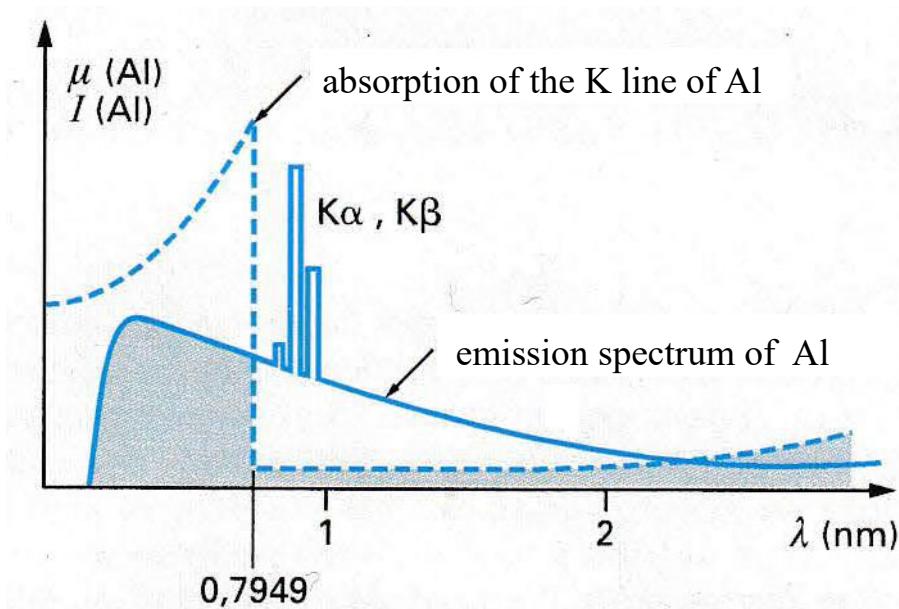
- ⇒ As for XRFS, the production of X-Rays is based on the interaction of electrons with the matter an especially through inelastic scatterings.
- ⇒ For XPS, the X-Ray tube is a Coolidge tube a slightly different from the one used in XRFS:



- ↳ The filaments are made of either pure tungsten or tungsten covered by some thorium, set at a tension from 5 to 20 kV.
- ↳ The anode can be made of an aluminium or a magnesium film (10 μm) deposited on a piece of copper.
- ↳ The choice of these two materials stems from the high intensity of the specific emission lines of these materials.
- ↳ The energies of the $\text{K}\alpha_1$ and $\text{K}\alpha_2$ of Al or Mg are high enough to excite most of chemical elements.

- ↳ Al and Mg give rise to a weak continuous spectrum which favours an Auger electron emission. The presence of Auger electron signals on an XPS spectrum can help the identification of the chemical elements present in a material.
- ⇒ It is also of interest to have a tube made of an anticathode composed by several metals like: Al/Mg or Cr/Si/Y.
- ↳ One advantage of exciting the same sample by several photons of different energies lies on the interpretation of the XPS spectrum, this method helps to distinguish the Auger and the XPS peaks.
- ↳ The XPS peak energy depends on the energy of the exciting X-Ray photon which is not the case for the energy of the Auger peaks.
- ⇒ Using an anticathode material which provides X-Ray photons of higher energy (Cr-K α instead of Al-K α) allows to probe a higher depth of the material which is translated into a bigger probed volume of the material.
- ⇒ In contrast, the use of the photon Zr-M ζ of lower energy will lead to an XPS analysis more sensitive to the surface of the material.
- ⇒ A window constituted by a thin metallic sheet of a few dozen of micrometer thick is used to isolate the tube from the sample chamber. This widow plays different roles:

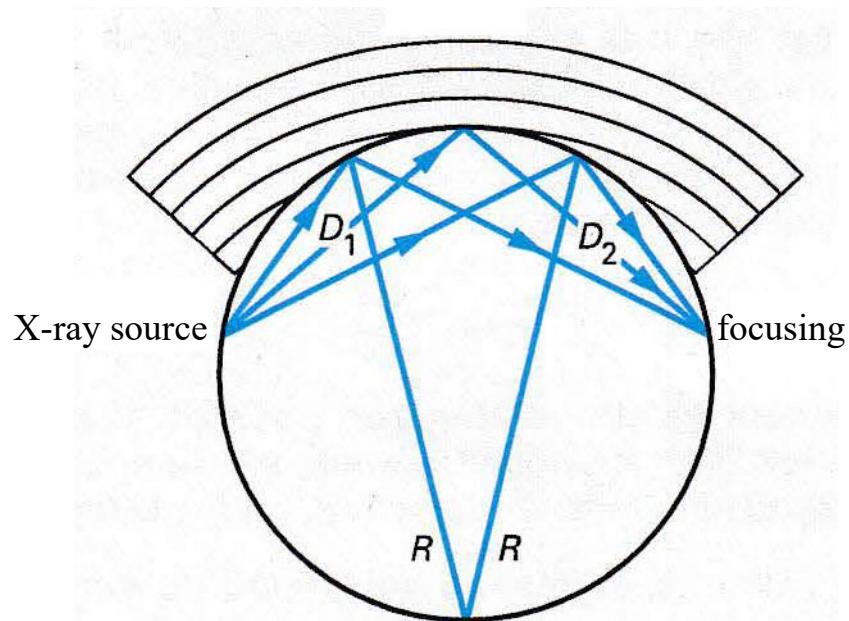
- ↳ Isolation toward the vacuum of the sample chamber which is better and cleaner than the one of the X-Ray tube
- ↳ Absorption matter toward secondary and backscattered electrons from the anticathode that will interfere with the analysed photoelectrons
- ↳ Energy filter of the emitted X-Ray beam by absorbing the high energy part of the bremsstrahlung. In general, the use of a metallic widow of the same chemical nature than the anticathode allows to achieve this goal without any alteration of the energy of the specific lines of emission of the anticathode:



excitation	Energy (eV)	FWHM (eV)
Mg-K α	1253.6	0.70
Al-K α	1486.6	0.85
Ti-K α	4510.0	2.00
Cr-K α	5417.0	2.10
Si-K α	1739.5	0.85
Zr-L α /Zr-M ζ	2042.4/151.4	1.70/0.77
He-I/He-II	21.2/40.8	<0.002/<0.002

X-Ray monochromator

- ⇒ The monochromator situated between the X-Ray tube and the sample is used to select the lines gathered in table given in slide 7.
- ⇒ The monochromator is based on a crystal of define interplanar spacing d which selects the emission line wavelength λ of interest according to the Bragg law.

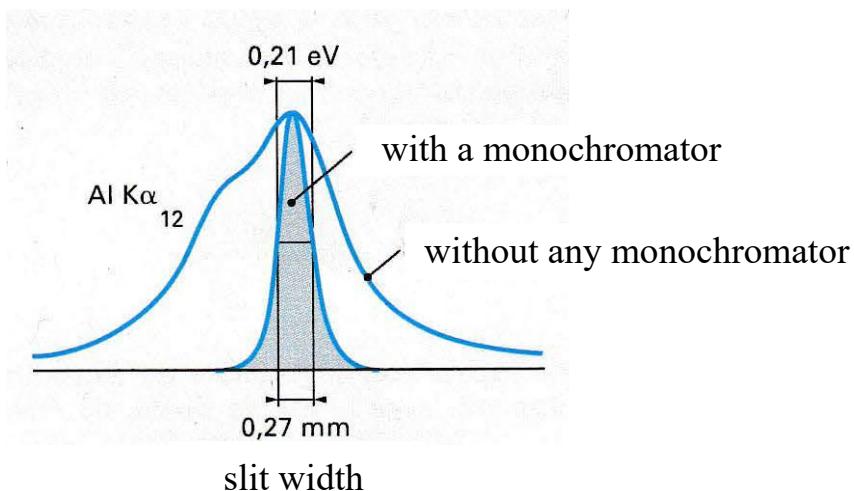


R is the Rowland circle radius and D_1 and D_2 are the focusing distances

$$n\lambda = 2d \sin \theta$$

- ↳ XPS instruments usually operate with a Johansson monochromator.
- ↳ The monochromator crystal is made of SiO_2 (1010) which is indicated for the selection of the $\text{Al-K}\alpha$ lines: $\lambda = 0.83 \text{ nm}$, $d = 0.425 \text{ nm}$ and $\theta = 78.5^\circ$.
- ↳ The curvature radius of the crystal is equal to the diameter of the Rowland circle.
- ↳ The emitted X-Ray beam spans from 30 to 400 μm diameter with a power up to 100 W.

- ⇒ The monochromator eliminates all the sources of interferences and ensures a clean XPS spectrum only obtained from the excitation of the selected X-Ray lines *e.g.* Al-K α .
- ↳ So the spectra from the satellites emission lines of the anticathode material, coming from the bremsstrahlung are eliminated. In addition, the monochromator acts also as a filter toward the possible emission lines coming from some impurities of the anticathode material (Cu, oxides from the anticathode material, contaminants...)
- ⇒ The monochromator reduces also the width of the emission lines of the X-ray tube and so improves the energy resolution of the spectrometer. It increases as well, the signal over noise ratio of the XPS peaks then given rise to a better sensitivity.



- ↳ It tends to reduce the intensity of the XPS signal but a good compromise between the energy resolution and the signal intensity is obtained with a width of 0.5 eV for Al-K α .
- ↳ It is also possible with the monochromator to reduce the spot size below 10 μm to provide a microanalysis spatially resolved.

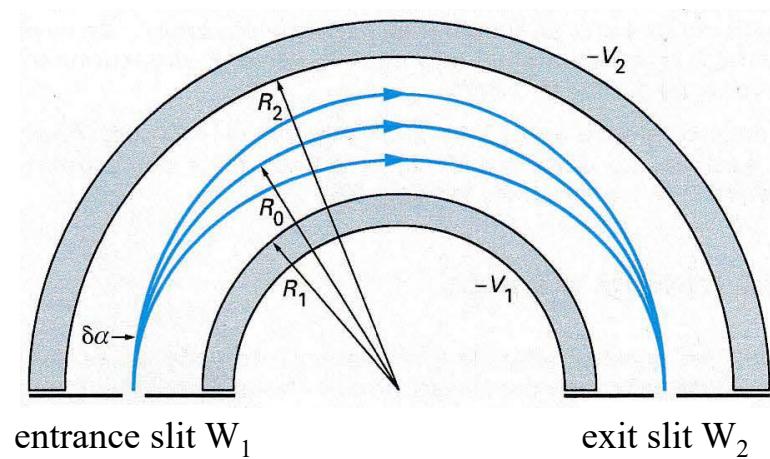
Electron focusing system

- ⇒ The main role of the electron focusing system is to collect the photoelectrons emitted by the sample and to transfer them to the analyser.
- ⇒ This system allows to ward off the analyser from the sample and so to let enough place in the sample chamber for the implementation of an etching device to clean up the sample or to remove superficial layer(s) of the material (studies by profilometry)...
- ⇒ This system is used to bring the electrons to the analysis energy E_a prior to be transferred to the analyser.
- ↳ To bring a photoelectron to E_a , one has to apply a delay potential R in agreement with its kinetic energy E_c .
- ↳ The tuning of R allows the determination of the kinetic energy of a given photoelectron which is the aim of an XPS measurement: $E_a = E_c - eR$
- ⇒ To achieve these goals, the electron focusing system is made of 5 to 10 electromagnetic lenses, each is optimised and has got a special function.
- ↳ The system can operate either in spectrometric or in imaging mode.

- ↳ Spectrometric mode: a high transmission level of the photoelectrons is required so the spatial resolution is worse as a maximum surface must be probed. The electrons image is produced with a magnification of about 5 times so with a non-optimal resolution.
- ↳ Imaging mode: the magnification of the produced images varies from 16 to 32 times. The transmission of the photoelectrons is reduced but the lateral resolution is improved.

Electron spectrometer

- ⇒ The electron spectrometer is usually made of an electrostatic prism, *i.e.* concentric hemispherical analyser CHA:



↳ The CHA is at 180° . Two concentric hemispheric glass tubes coated with gold generate an electric field when applying different electrical negative potentials ($-V_1$ and $-V_2$).

↳ The energy of analysis E_a is proportional to $\Delta V (> 0)$:

$$E_a = ke(V_2 - V_1)$$

- ↳ k is the spectrometer constant: $k = (R_2/R_1 - R_1/R_2)^{-1}$.
- ⇒ The spectrometer operates at a fix E_a . The scanning of the kinetic energy of the emitted photoelectrons is obtained by the tuning the delay potential R .
- ↳ At each R value corresponds a kinetic energy of a photoelectron which is related to the nature of the emitted element and its electronic environment.
- ↳ In this mode, the energy resolution is optimised.

Electron detector

- ⇒ The electron detector is based on a channeltron (an electron multiplier, see the chapter concerning the matter emission). The spectrometer can be equipped with up to 10 channeltrons.
- ⇒ Another alternative consists in a network of tubular microchannels of 15 to 25 μm of diameter.
- ↳ The electrons are channelled in the microchannels and are emitted with an amplification factor of about 10^5 .
- ↳ They are collected by a system made of resistive anodes.

Sample

- ⇒ The sample size is from 0.5 - 1 cm² and up to 4 mm thick. The analysis of thicker samples requires a special holder.
- ⇒ As the principle of a XPS instrument is based on the signal given by electrons, it requires an ultrahigh vacuum. The sample chamber is at 10⁻¹² Bar so it imposes a high vacuum constraint on the studied sample.
- ⇒ As a high conductivity of the studied material is not mandatory, it is possible to analysis insulator materials by XPS, nevertheless charging effects are somewhat important.
 - ↳ Actually, the emission of the photoelectrons creates some positive charges which for insulators are not drain, so leading to the positive charging of the material surface.
 - ↳ This positive potential slows down the emitted photoelectrons and so displace their measured binding energies towards higher values.
- ⇒ The analysis of magnetic samples can cause troubles to the photoelectron focusing system due to its electromagnetic lenses.
 - ↳ The analysis of magnetic samples requires a special tuning of the photoelectron focusing system.

Qualitative analysis

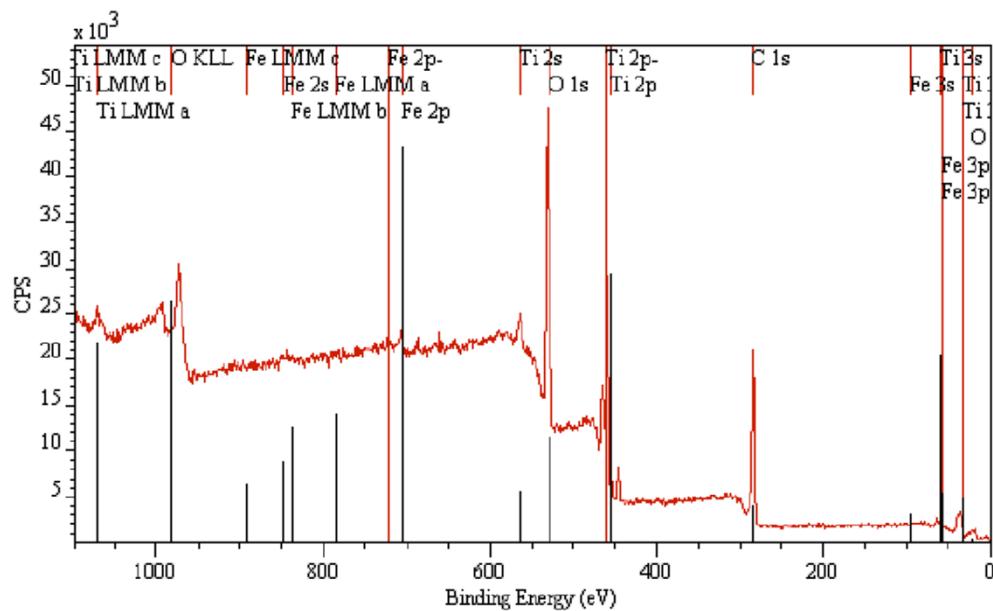
General features

- ⇒ The ionisation of the matter, leading to the photoelectron generation includes the matter relaxation which generates specific X-Ray and Auger electron emissions.
- ⇒ XPS is based on the measurement of the kinetic energy of the ejected photoelectrons upon an X-Ray irradiation of a few keV.
- ⇒ The resulting XPS spectrum is made of lines, the energy of which are the bonding energies of the collected photoelectrons which are defined by the chemical nature of the emitting components.
- ⇒ The XPS analysis is altered by the presence of a continuous secondary electron background due to the inelastic scattering underwent by the photoelectrons with the surrounding matter.
- ⇒ Compared to the excitation of the core electrons, the excitation of the electrons of the valence bond is rather weak in XPS.
- ⇒ In the typical domain of exciting energy applied to XPS, the X-Ray photons interact mainly via the photoelectric effect.

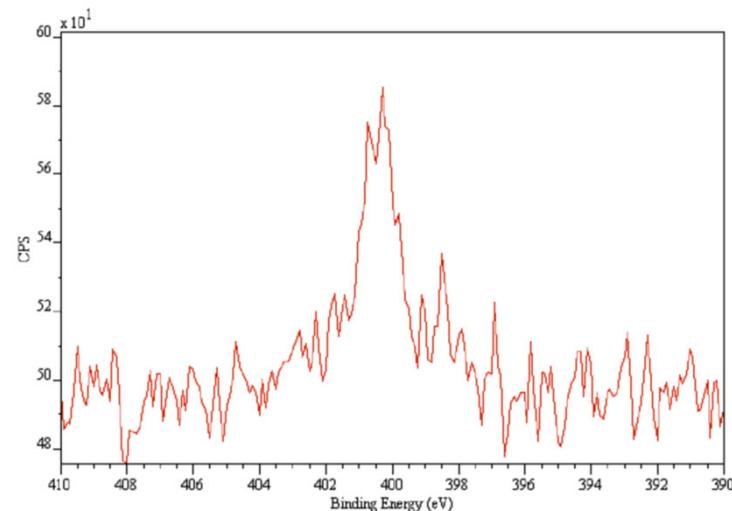
- ⇒ The XPS lines are labelled according to the combination of the name of the chemical element and the photoelectron nature: C1s, O2s, C2p^{1/2}...
- ⇒ The XPS spectrometer is calibrated in energy, so the XPS lines are directly labelled as C1s, O2s, C2p^{1/2}...
- ⇒ The excitation energy of the material is around 1.5 keV (1486.6 eV for Al-K α and 1253.6 eV for Mg-K α).
- ⇒ This excitation energy allows the ionisation of the 1s level of the elements of the second period but is not enough to ionise the 1s level of the other elements.
- ⇒ For the elements with a principal quantum number $n \geq 3$, the ionisation takes place by interaction with electrons 2p, 3d, 4d or 4f...
- ⇒ XPS can probe all the elements except H and He which do not possess specific shell levels.
- ⇒ Except for very light elements, a chemical element exhibits more than one XPS line that allows a easier determination of this chemical element. An XPS line spans from 0.1 to 5 eV.
- ⇒ The principal XPS line, the one pertaining to the ionisation of the electron presenting the lower set of quantum numbers is the most intense. Its FWHM is typically around 1 eV.

XPS mechanism

- ⇒ As already mentioned, an XPS measurement correlates directly the energy of the analysed photoelectrons to the energy levels of the target atom.
- ⇒ As an example, a typical XPS spectrum is given below:



→ The presented spectrum, corresponds to the analysis of a TiO_2 material modified with Fe and a protoporphyrin (C, H, N). The N1s signal situated at 400 eV is visible on the magnified spectrum:



⇒ The characteristic kinetic energy E_{c_0} of the photo-electron depends on the energy $E_0 = h\nu_0$ of the exciting photon and on the binding energy W_x of the target core electron X:

$$E_{c_0} = h\nu_0 - W_x = E_0 - W_x$$

↳ The ionisation energy of the photoelectron is also known as the binding energy E_L :

$$E_{c_0} = h\nu_0 - E_L$$

↳ The Koopmans approximation considers only the ejected electron, the other electrons being "frozen" *i.e.* are not affected by the photoionisation process. Then the binding energy is equal to the energy of the target electron, calculated according to the Hatree-Fock model:

$$E_{c_0} = h\nu_0 + E_{HF}$$

↳ To take into account the perturbation caused by the ionisation of the considered atomic level, the Koopmans ionisation energy is corrected by a relaxation term $E_{relax} (> 0)$ as:

$$E_{c_0} = h\nu_0 + E_{HF} - E_{relax}$$

- ↳ The relaxation energy E_{relax} is subdivided in two terms, an intra- and an extra-atomic relaxations.
- ↳ In XPS, only the extra-atomic relaxation which arises from the electrons of the surrounding atoms and/or from the whole solid (valence band and conducting band electrons) contributes specifically to the energy shift of the XPS lines.
- ↳ The intra-atomic relaxation is constant for a given atom whatever its chemical environment.
- ⇒ The chemical shift, that is the displacement of the XPS lines, is a consequence of the ionisation state of the target element and its relaxation across the chemical nature of its neighbours.
- ↳ The determination of the chemical shift of a given element in a material leads to the determination of its oxidation state and to the determination of the chemical and bond natures of its linked partners.
- ⇒ After ejection, the photo-electrons must migrate from the bulk material to its surface.
- ↳ During this migration, they can interact across elastic and inelastic scatterings with the electrons of the surrounding chemicals.

- ↳ To leave the material, the photo-electrons must also counteract the potential barrier Φ_{sa} at the material surface.
- ↳ In addition, the photoelectrons when entering the spectrometer can be accelerated or decelerated according to Φ_{sp} related to the extraction energy of the spectrometer.
- ↳ The real kinetic energy of a given photoelectron is then:

$$Ec_0 = h\nu_0 + (E_{HF} - E_{relax}) + e(\Phi_{sa} - \Phi_{sp})$$

- ↳ The proper calibration of the spectrometer in kinetic energy using standards like pure silver or gold, that is the determination of Φ_{sp} , allows the precise determination of the kinetic energy of a given photoelectron.

Affecting phenomena

- ⇒ Several phenomena can affect the position and/or the shape of an XPS signal.

Charging effects

- ⇒ For insulating samples, the ionisation of the sample which causes a positive charge increase of the matter is not drain.
- ↳ The appearance of this positive potential at the material surface slows down the emitted photoelectrons and so the XPS peaks are displaced toward more positive energies.
- ↳ In addition, this potential which is not homogeneous along the surface increases the width of the XPS peaks.
- ↳ If this potential migrates to the bulk of the material it can cause the duplication of the XPS signals of a given element.
- ⇒ When the charging effect is weak, it is possible to measure the displacement of the peaks of standards used to rescale the whole XPS spectrum.
- ↳ A thin film of gold can be deposited on the sample and the calibration is based on the Au 4f^{7/2} peak.
- ↳ One can also use the C1s peak coming from CO₂ naturally adsorbed on all the samples as a calibration standard.

- ⇒ When the charging effect is too big, a possibility remains into the use of a flood gun that delivers some electrons to the sample to kill its positive charging.
- ⇒ One has to be careful in determining the electron flux delivered to the material as an excess of electrons at the material surface will accelerate the emitted photoelectrons and so the XPS peaks will be displaced towards more negative energies.

Peak asymmetry

- ⇒ For a majority of chemical elements, the XPS peaks are symmetric either corresponding to a Gaussian or to a Lorenzian function or to a mixture of both.
- ⇒ Asymmetry for metal samples arises from the excitation of the conducting band electrons during the photoelectron emission.
- ⇒ For insulators, the charging effects are responsible for the broadening of the peaks.
- ⇒ For insulators, a chemical heterogeneity can cause different chemical shifts below 0.5 eV (below the spectrometer energy resolution) on the same element that will provide a peak shoulder.

Background caused by secondary electrons

- ⇒ At each XPS peak is associated a background signal due to the secondary electrons. This background has a kinetic energy lower than the one of the associated peak.
- ⇒ This background is due to the photoemission process when the emitted photoelectrons interact through inelastic scatterings with the surrounding matter, causing the ionisation of some chemical elements along their pathway to the material surface.
- ↳ After several interactions, the photoelectrons leave the material with a weaker kinetic energy than expected.
- ↳ As these interactions are not quantified it leads to a continuous kinetic energy spectrum of secondary electrons that constitutes this background.
- ⇒ The intensity of this background is also associated to the location of the emitting elements.
 - ↳ For emitting elements situated near the surface, the background is rather weak.
 - ↳ For emitting elements situated farther from the surface, the background is more intense.
 - ↳ For emitting elements situated in the bulk material, the photoelectrons are trapped in the material and will never reach the surface.

- ⇒ The area of the principal XPS peak of a given element contains only a few contribution of secondary electron background.

Multiple structure of the XPS peaks

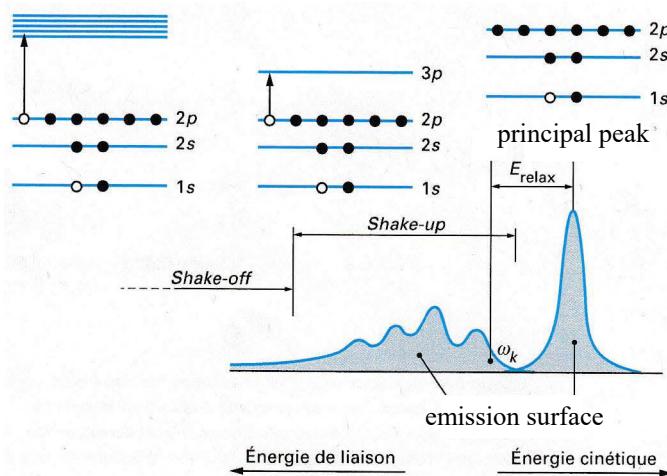
- ⇒ The XPS spectra do not show only simple peaks.
- ⇒ The connection between the monoelectronic atomic orbitals and the resulting peaks is not always respected.
- ↳ In many cases, the XPS lines present multiple structures and satellite peaks.

Multiplets of spin

- ⇒ The XPS spectra of paramagnetic compounds show some splitted lines (multiplets).
- ↳ This phenomenon is particularly important for 3d elements.
- ↳ These multiplets are explained by the spin exchange interactions between the vacancy left by the departure of the photoelectron and the unpaired electrons d and f of the valence band of the material.

Shake-up peaks and shake-off background

⇒ One of the consequence of the effects of the relaxation due to ionisation of the core level of a target element is the appearance of satellite peaks called shake-up peaks and the presence of a shake-off background.



- ↳ The principal peak is related to the ionisation of the target element.
- ↳ The shake-up peaks are related to the relaxation energy communicated to several valence electrons leading to several peaks.
- ↳ The Shake-off background is related to the relaxation energy communicated to the free energy continuum of the material.

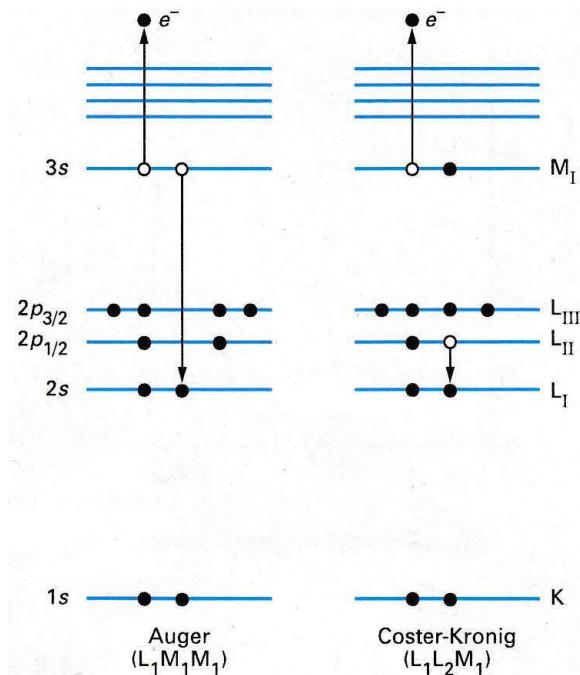
Peaks coming from energy loss

- ⇒ During the emission of the photoelectrons, the simultaneous excitation of several plasmons in metals and semiconductors or interband transitions in insulators can occur.
- ⇒ The energy of the emitted photoelectrons is then lowered and then some satellite peaks corresponding to these photoelectrons appear on the XPS spectrum around the principal peak. These peak are known as energy loss peaks.

Auger transitions

- ⇒ During the relaxation of the matter, Auger electrons are emitted and are detected as intense lines in the XPS spectrum.
- ⇒ As for the photoelectrons, the Auger electrons are sensitive to the chemical environment of the emitting element thus leading to a chemical shift.
- ⇒ This chemical shift can be explored in correlation with the chemical shift of the XPS peaks to improve the determination of the bonded partners of a target element.
- ⇒ In contrast with photoelectrons, the kinetic energy of the Auger electrons is independent of the energy of the exciting X-Ray.

→ Below are depicted the emission of Auger electrons after ionisation of the level L_I :



→ 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:

$$Ec_0(Z) = W_x(Z) - W_y(Z) - W_{y'}(Z+1)$$

→ $W_{y'}(Z+1)$ is introduced to take into account that the Auger electron is ejected from an ionised atom.

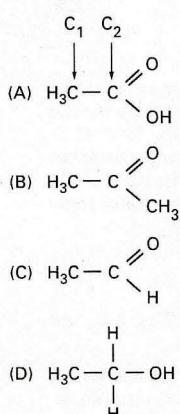
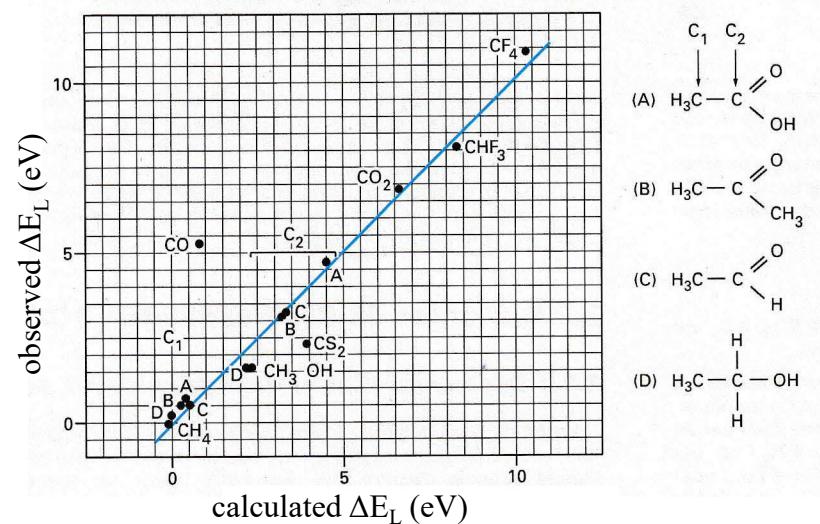
→ As for the photoelectrons, taking into account the extraction potentials of the sample and the spectrometer, the kinetic energy of an XYY' Auger electron reads:

$$Ec_0 = W_x(Z) - W_y(Z) - W_{y'}(Z+1) + e(\Phi_{sa} - \Phi_{sp})$$

- ⇒ Changing the wavelength of the excitation beam allows to distinguish XPS and Auger lines.
- ⇒ Combining the chemical shifts measured for XPS and Auger signals in a common spectrum allows a better determination of the bonded neighbours of a probed element.

Interpretation of the XPS spectra

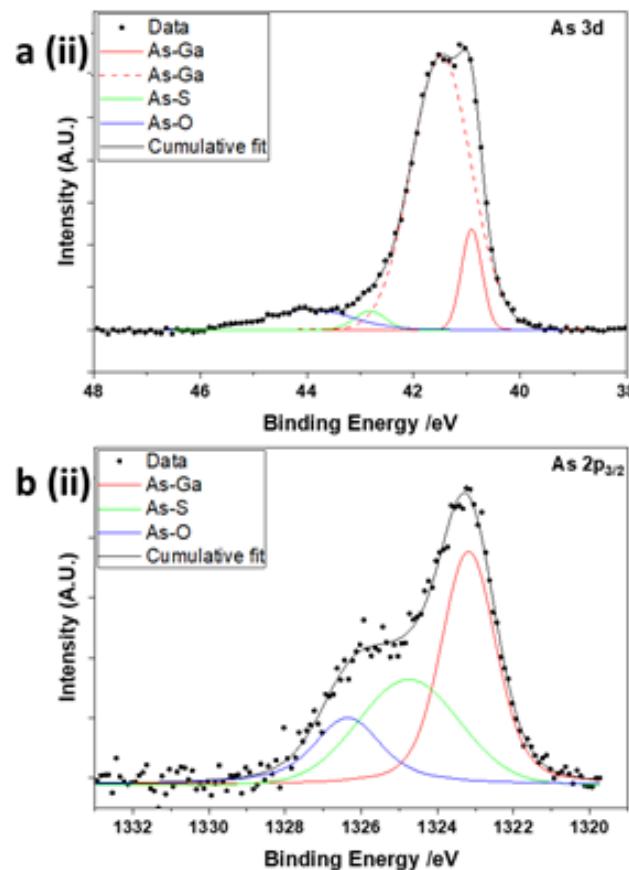
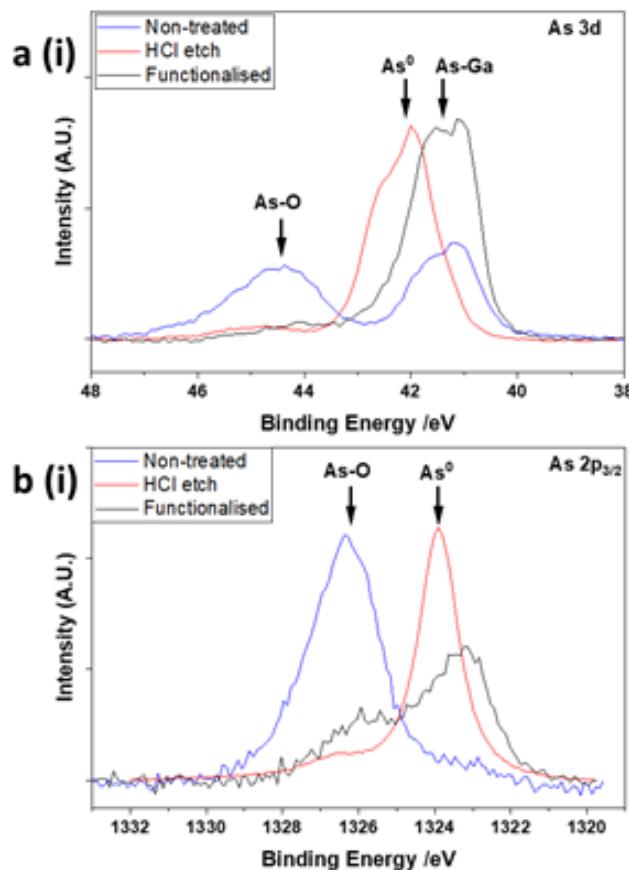
- ⇒ The interpretation of a XPS spectrum is mainly based on the chemical shift.
- ⇒ A model, based on a electrostatic potential is used to quantify the variation of the binding energy ΔE_L as a function of the chemical environment of the probed element. This model offers a nice correlation with the observed ΔE_L :



$$\Delta E_L = 14.4 \left(\frac{q_i}{r_i} + \sum_j \frac{q_j}{r_{ij}} \right)$$

↳ q_i is the charge (C) of the target atom *i* of radius r_i (Å) and q_j are the charges (C) of the surrounding neighbours separated from the target atom by the distance r_{ij} (Å).

→ Below are the XPS spectra of non-functionalised and functionalised GaAs semiconducting electrodes. The functionalisation consists in the grafting of a biphenyl layer at the GaAs surface.



↳ Series (i) correspond to the obtained spectra.

↳ Series (ii) are the deconvoluted signals of Arsenic.

↳ The chemical shifts on Arsenic induced by its bonded partners are clearly visible.

⇒ The XPS setup parameters are as follows:

- ↳ The Analyses were performed using a monochromatic Al K α X-ray source at 24.8 W power.
- ↳ The beam size was 100 μ m.
- ↳ The spectra were corrected for C-1s (C-C) peak at 285.0 eV.
- ↳ The pass energy was 20 eV yielding a full width at half maximum of 0.70 eV for the Ag 3d 5/2 peak.
- ⇒ The XPS investigations were firstly carried out with a pass energy of 46.95 eV yielding a full width at half maximum of 0.91 eV for the Ag 3d 5/2 peak.
- ↳ It resulted in XPS data with a poor resolution which did not allow a reliable deconvolution of the core-level signals and the correct identification of the various species present in the As-3d spectral regions.
- ↳ Decreasing the pass energy from 46.95 eV to 20 eV allowed a better resolution compatible with an accurate deconvolution process.

Quantitative analysis

General features

- ⇒ The typical probed depth varies from 0.4 to 5 nm.
- ⇒ This typical depth can be enhanced by tilting the angle of analysis of the emitted photoelectrons (not perpendicular to the sample).
- ⇒ Another possibility remains into the use of X-Rays of variable energies. The excitation with anticathodes made of Zr-M ζ , Al-K α and Cr-K α allows the analysis at 3 different depths: 0.5 nm, 2.5 nm and 5.0 nm respectively.
- ⇒ To perform a concentration profile one can use an ionic etching with a beam of argon ions Ar $^+$. Nevertheless, this method can introduce some chemical artefacts.

Method of the factor of elementary sensibility

- ⇒ This method is based on the use of a data base made of pure compounds or compounds of very well defined stoichiometry for which the intensity of a given XPS line (e.g. As 3d) is measured and noticed I $^\infty$.

⇒ The relative atomic concentration $C_{ra,i}$ of an element i in a material is related to ratio of one of its XPS line intensity I_i other the intensity I_i^∞ of the same XPS line for the pure element i . This value is divided by the sum of the relative intensities of the other components as:

$$C_{ra,i} = \frac{I_i / I_i^\infty}{\sum_j I_j / I_j^\infty}$$

⇒ The limits of detection (LOD) and quantification (LOQ) for an element i are related to the counting time t_c (s), the intensity $I_0(i)$ of a given XPS line of a pure standard of i (counts) and the intensity I_b of the background noise (counts), C_0 being taken as 10^{23} atoms per cm^3 :

$$\text{LOD}(i) = C_0 \frac{3}{\sqrt{t_c} \sqrt{I_0(i)} \sqrt{I_0(i)/I_b}} \quad \text{and} \quad \text{LOQ}(i) = C_0 \frac{10}{\sqrt{t_c} \sqrt{I_0(i)} \sqrt{I_0(i)/I_b}}$$

⇒ The limit of detection is about 0.1% atomic which corresponds to a LOD in volume of 10^{20} atoms per cm^3 and to a LOD in surface of 10^{12} atoms per cm^2 . The precision of the quantification is about 3% atomic percentage.

Analytical features of XPS

⇒ The following table gathers the principal features of XPS:

technic	input beam	d_B (μm)	depth (μm)	z_X	LOD (ppm)	precision (atomic %)
XPS	X-Rays	10 - 400	0.5 - 5×10^{-3}	$\geq \text{He}$	1000	1 - 3