Last name :
First name :
Exam room :
Seat number :

Exam of Physical and Chemical Analyses of Materials

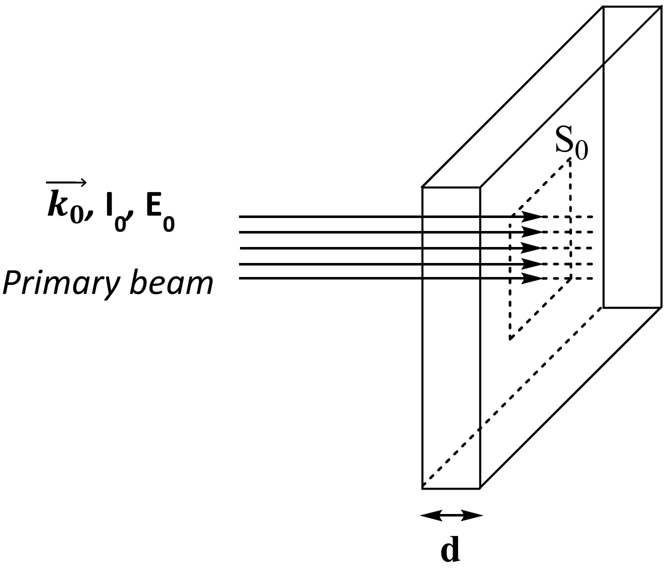
June 2024

Duration: 3 hours

I. Interaction beam-matter

I.1. Interaction beam-matter: matter excitation

During a physical or a chemical analysis of a material, one has to take into account the interaction of a beam with the matter across a surface $\mathbf{S_0}$. The primary beam is characterized by a wave vector $\overrightarrow{\mathbf{k_0}}$, a beam energy $\mathbf{E_0}$ and a beam intensity $\mathbf{I_0}$. After interacting with the matter, the primary beam is affected by the different events.



Complete the table by ticking the box(es) which correspond(s) to the parameter(s) mainly affected by the following events:

	$\overrightarrow{k_0}$	$\lVert\overrightarrow{k_0}\rVert$	E_0	I_0
Absorption				X
Elastic scattering	X			X
Inelastic scattering	X	X	X	X

Complete the following table related to the use of electrons and X-Rays as primary beams:

Event	Nature of the primary beam	Type of scattering	Target
Rayleigh	*X-Rays*	*Elastic*	*Whole electronic cloud*
Compton	*X-Rays*	*Inelastic*	*electrons*
Bremsstrahlung	*Electrons*	*Inelastic*	*nuclei*
Diffraction	*X-Rays or Electrons*	*Elastic*	*Whole electronic cloud (nuclei location)*
Ionisation	*X-Rays or Electrons*	*Inelastic*	*electrons*

Indicate if the following statements are true or false:

	true	**false**
▪ The modulus of the wave vector is not linked to the energy of its associated particle.	☐	■
▪ The cross-section for the Compton effect increases with the energy of the X-Ray photons.	■	☐
▪ The Bremsstrahlung generates specific X-Rays.	☐	■
▪ Diffraction occurs when the wavelength of the incoming beam and the diffracting object have almost the same size.	■	☐
▪ The ionisation of a target atom always takes place at the K level.	☐	■

I.2. Interaction beam-matter: matter emission

Complete the following table while considering inelastic scatterings leading to the ionisation of the matter. Indicate if the emission is directly caused by the primary beam (direct emission) or consecutive to the matter relaxation (indirect emission) by ticking the correct(s) box(es).

Primary beam	**Emission type**	**Direct emission**	**Indirect emission**
X-Rays	***Photo-electrons***	**X**	
	X-Rays		**X**
	Auger electrons		**X**
Electrons	***Secondary electrons***	**X**	
	X-Rays		**X**
	Auger electrons		**X**

In material analysis, the emission types listed above are used for either microscopic or analytical purposes.

Among the emission types listed above, highlight the one(s) which possesses/possess an energy related to the energy of the primary beam.

Photo-electrons

Among the emitted beams listed above, highlight the one(s) which possesses/possess an energy only related to the chemical nature of the emitting element.

X-Rays and Auger electrons

Among the emitted beams listed above, highlight the one(s) for which it is not clearly possible to correlate its energy to neither the energy of the primary beam nor the chemical nature of the emitting element.

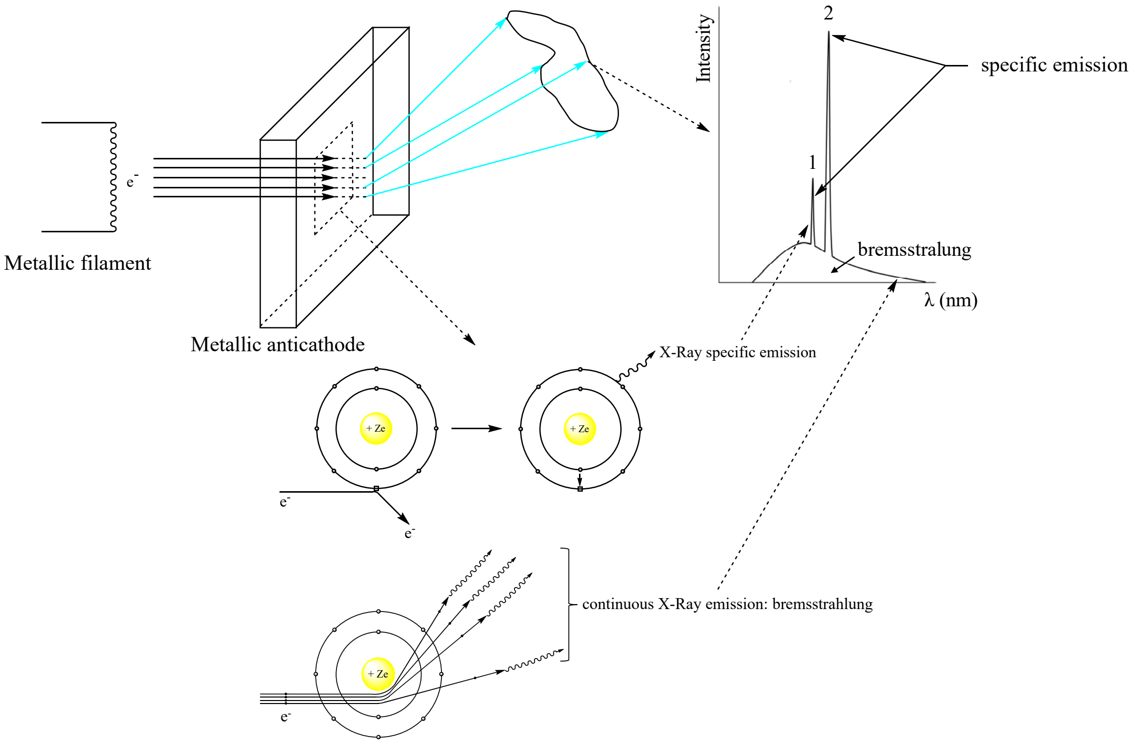
Secondary electrons

Indicate if the following statements are true or false:

	true	**false**
▪ The probability of X-Ray emission is greater for light chemical elements than for heavy ones.	☐	■
▪ The emission of X-Rays follows strict selections rules.	■	☐
▪ Auger electrons can be produced by either an X-ray or an electron primary beam.	■	☐
▪ The kinetic energy of Auger electrons is correlated to the energy of the primary beam.	☐	■
▪ The emission of Auger electrons follows strict selection rules.	☐	■

I.3. Interaction beam-matter: X-rays production

XRF and XPS instruments share the same primary beam, that is X-Ray photons. Using a drawing, describe how X-Rays are produced. Indicate on the drawing the mechanism(s) that produces/produce X-rays during the interaction beam-matter using a simple Bohr atom model. Draw the resulting X-ray spectrum: the intensity **I** of the X-Ray photons as a function of the wavelength **λ**.



II. Physical characterization of materials

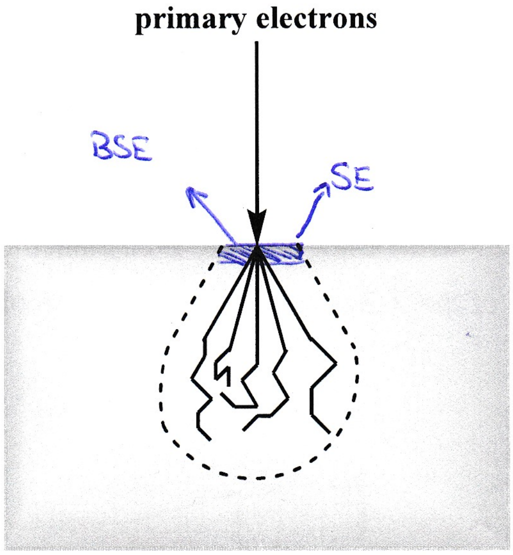
II.1. Electron microscopy

SEM (Scheme **A**) and TEM (Scheme **B**) are both related to electron microscopy. Complete the following drawings with:

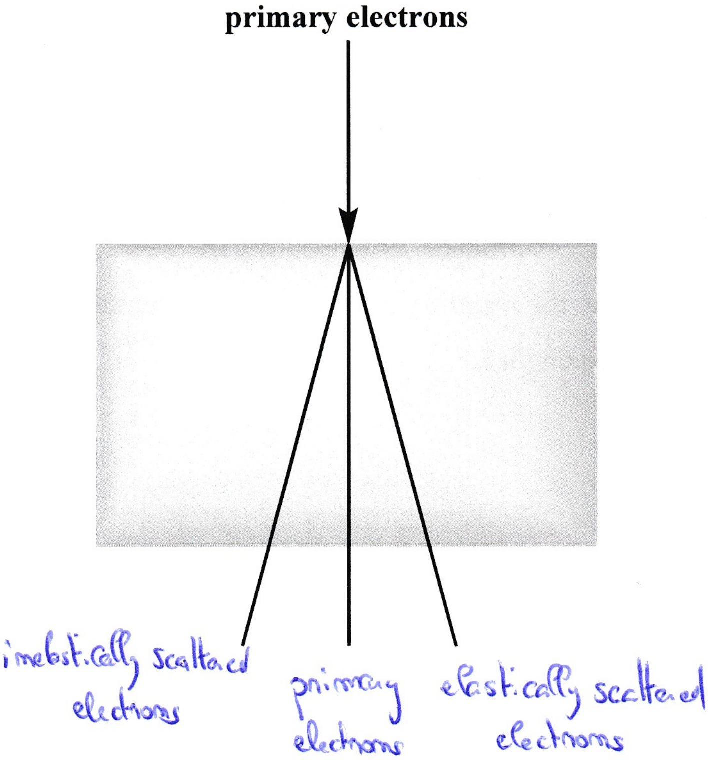
- the trajectory of the electrons in the studied sample and the specific probed sample volume

- the events recorded for each microscopy and the emission zones of these events

Scheme A: SEM



Scheme B: TEM



Based on the previous question, complete the following table and thick the correct answer(s).

	TEM	**SEM**
Typical beam energy range	***100 to 200 keV***	***0.1 to 30 keV***
Lateral resolution range	***Angstöm***	***Namometer***
Scanning mode	☐ yes ■ no	■ yes ☐ no
Sample features	■ size ≤ 3 mm ■ thickness < 100 nm ☐ high surface conductivity ☐ flat surface ■ specific preparation	☐ size ≤ 3 mm ☐ thickness < 100 nm ■ high surface conductivity ☐ flat surface ☐ specific preparation
Sample holder	☐ conducting holder ■ no requirement	■ conducting holder ☐ no requirement
Analysed signals	***Transmitted electrons***	***Secondary electrons*** ***Backscattered electrons***
Type(s) of image	***Diffraction pattern*** ***HRTEM*** ***BF image*** ***DF image***	***Secondary electrons image*** ***Backscattered electrons image***

What is the main effect while reducing the energy of the electron primary beam?

Degrading the lateral resolution because the resolution is inversely proportional the wavelength of the primary beam so directly proportional to the primary energy.

In which type of electron microscopy and for which reason(s) it may be sometimes of interest to decrease the energy of the primary electron beam?

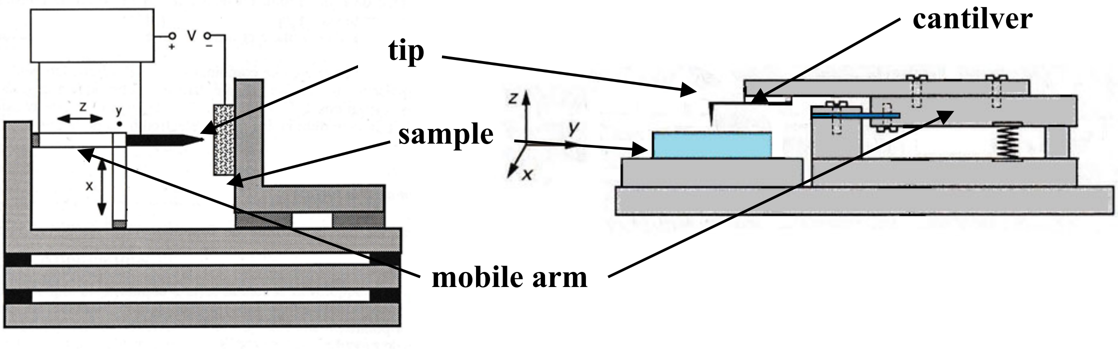
Actually, in SEM when the studied sample is not conducting enough, one can observe the accumulation of electrons at the surface that will causes the blurring of the image and at least the defocusing (loss of image sharpness) and finally the reflection (blinding of the detector)of the primary electron beam. To counteract this problem, a possibility remains into the decrease of the primary electron beam to decrease the accumulation of electrons at the surface of the studied sample. Except the degradation of the lateral resolution and so the sharpness of the image, it will enhance the production of SE and AE so providing more surface details.

Indicate if the following statements are true or false:

	true	**false**
▪ With TEM, it is possible to obtain morphological information on nanoparticles deposited on an electron transparent material.	■	☐
▪ With TEM, it is possible to obtain morphological information on a bulky material.	☐	■
▪ With TEM, it is possible to obtain structural information on an amorphous material.	☐	■
▪ With TEM, it is possible to obtain topographical information using the method of replicas.	■	☐
▪ For SEM studies, the sample must be prepared using the Formwar method.	☐	■
▪ In SEM, decreasing the beam energy enhance the production of backscattered electrons.	☐	■
▪ In SEM, a sample coating made of gold enhances the production of secondary electrons.	■	☐
▪ In SEM, charging effects appear when the electrons at the surface of the material are correctly drained.	☐	■

II.2. Scanning probe microscopy

Below are depicted the technical schemes of an AFM and a STM microscopes. Appoint each microscope to the corresponding scheme.



A: STM **B: AFM**

Indicate on the schemes above the location of the sample, the tip, the cantilver and the mobile arm.

Complete the following table by ticking the correct box(es):

	STM	AFM
Tip directly mounted on a mobile arm	X	
Tip indirectly coupled to a mobile arm		X
Tip polarised against the studied material	X	
Setting up a tunnelling current between the tip and the studied sample	X	
Setting up a contact between the tip and the studied sample		X
Sensitive to the forces involved between the tip and the material		X
Sensitive to the electronic states of a material	X	
Analysis of conductors and semiconductors	X	X
Analysis of insulators		X
Lateral resolution at the Angstrom level	X	
Lateral resolution at the nanometre level		X

What is the difference between an STM image obtained from a positive mode (the tip is positively polarised against the sample) and from a negative mode (the tip is negatively polarised against the sample)?

When the tip is positively polarised against the sample, the image corresponds to the iso-density of the electronic states at the energy of the Fermi level EF representing the filled surface states.

When the tip is negatively polarised against the sample, the image will then correspond to the iso-density of the electronic states at an energy higher than the fermi level (EF + ε) representing the empty surface states.

Which scanning probe microscopy would you choose to study a biological membrane?

Actually, based on the fact that a biological membrane is an insulating material, I would turn to AFM which is fully dedicated to the study of every kind of material whereas STM, because of the establishment of tunnelling current requires some conducting properties from the studied sample.

With which mode are you going to operate? Base your answer on a brief description of the chosen mode while pointing out its highlights regarding the nature of a biological membrane.

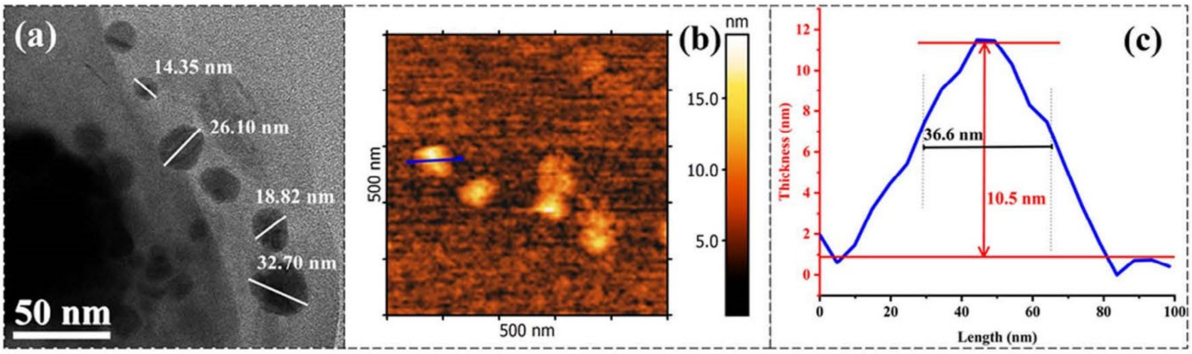
Regarding the running mode, I would rather prefer a taping mode because of the soft nature of the studied sample: Briefly, the tip oscillate at a given amplitude and frequency and the latest is further moved along the surface. The height of the mobile arm is tunned along the z axis to maintain the amplitude of the oscillations leading to a surface profile. The intermittent contact between the tip and the sample in a taping mode is then ideal because it will decrease a lot the influence of the lateral forces that can arise from a contact mode and that will further degrade the sharpness of the image.

Indicate if the following statements are true or false:

	true	**false**
▪ STM is always performed under vacuum or under inert atmosphere.	■	☐
▪ The STM tip is still along the x and y axes.	☐	■
▪ STM can be performed at constant height.	■	☐
▪ STM can be performed at a constant tip oscillation amplitude.	☐	■
▪ AFM is mostly used for morphological studies.	☐	■
▪ The AFM tip is moving along the scanned surface.	☐	■
▪ AFM performed in contact mode is dedicated to the study of soft surfaces.	☐	■
▪ The STM tip can oscillate at a given frequency.	☐	■
▪ When AFM is performed in tapping mode, the tip is in intermittent contact with the scanned surface.	■	☐

II.3. TEM versus STM

STM and TEM achieve almost the same lateral resolution and then can be compared. Below are displayed the analysis of MgB_2 nanoparticles by TEM and STM:



A) TEM image of the synthetised nanoparticles, **B**) STM image of the synthetised nanoparticles, **C**) resulting topography of a given synthetised nanoparticle.

What kind of TEM image is displayed in figure **A**?

This is a BF image.

The STM image was recorded at a constant tunnelling current of 2 nA. Briefly describe this operating mode.

In a constant tunnelling current approach, the tip of the STM will follow the topography of the scanned sample by adjusting its position along the z axis to conserve the current intensity. The resulting image will represent the distance between the tip and the scanned surface along the x and y axes.

Briefly describe the TEM and STM pictures in terms of morphology and topography.

From a morphological point of view, looking at the TEM picture displays on figure a, one can see a sharp image of the contour of the nanoparticles thus highlighting the morphological character of the TEM analysis. In contrast, when looking at the STM picture of the same nanoparticles, one can observe that the contour of these particle is blurred.

From a topographic point of view, the only manner to access to such information by TEM is to use the replicas (direct or indirect replicas) and to rebuilt an image by means of the series of shots taken from the replicas. In contrast, as said before, STM run in a constant current mode is fully dedicated to grasp the topography of a surface as the image displays the distance between the tip and the surface along the scanning x and y axes.

The topographic profile displayed on figure **c** relies on which technic: TEM or STM?

According to the previous answers, we can be pretty sure that the topography displayed on figure c was obtained from the STM analysis.

III. Chemical characterization of materials

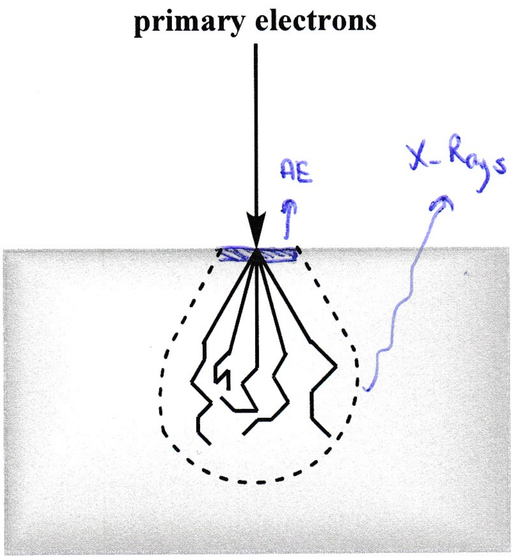
III.1. General

Chemical analysis of a material are mainly carried out using electron or X-ray sources.
Complete the following drawings with:

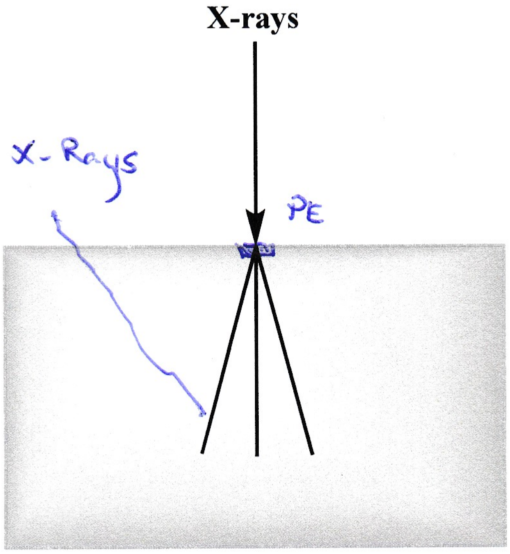
- the trajectory of the primary beam in the studied sample and the specific probed sample volume (in both cases, the primary beam does not emerge from the sample).

- all the events related to analytical purposes and the emission zones of these events.

Scheme A



Scheme B



Indicate if the following statements are true or false:

	true	**false**
▪ Secondary electrons are considered for chemical analysis.	☐	■
▪ Backscattered electrons are considered for chemical analysis.	☐	■
▪ Useful electrons in chemical analysis are emitted from the surface of the material.	■	☐
▪ For chemical analysis, the brightness of the electron source is of most importance compared to its stability.	☐	■
▪ For chemical analysis Hard X-Ray sources are required.	☐	■

In analytical chemistry, the proposed analytical method must meet two different features. What are these two features?

The method must be qualitative and quantitative.

III.2. Bulk and surface analyses

Complete the following table by ticking the correct box for each chemical analysis:

	Semi-Bulk	**Bulk**	**Surface**
XRFS		**X**	
XPS			**X**
XRMA	**X**		
AES			**X**

Complete the following table by ticking the correct box for each chemical analysis:

	X-ray as primary beam	**Electrons as primary beam**
XRFS	**X**	
XPS	**X**	
XRMA		**X**
AES		**X**

Complete the following table by filling the boxes:

	Background signal	**Recorded signal**	**Side signal(s)**
XRFS	***Bremsstrahlung***	***Specific X-Rays***	***X-Rays from the anticathode*** ***X-Rays from Compton effect***
XPS	***Secondary electrons***	***Photo-electrons*** ***Auger electrons***	***none***
XRMA	***Bremsstrahlung***	***Specific X-Rays***	***none***
AES	***Secondary***	***Auger electrons***	***Backscattered electrons***

XRMA can be achieved thanks to an SEM or using a specific apparatus.

Give the name of this specific apparatus.

Electron Micro-Probe analyser EMPA

What are the differences between the electron sources of these two apparatus?

The two electron sources differ from the fact that the electron gun is different: W for EMPA whereas a LaB6 or a FEG is used in EM. In addition, there is a stabilizing device included in the electron column of the EMPA that stabilizes the intensity of the primary beam. Last, in term of energy, for SEM one can go up to 30 keV whereas for EMPA, on can go up to 50 keV.

Briefly describe the spectrometer associated to each apparatus?

In SEM, the spectrometer is constituted by a single device, the detector which plays the role of analyser and detector. It indeed gives both qualitative and quantitative information. In EMPA, the spectrometer is constituted by two devices an analyser made of a crystal analyser which select the different emission wavelengths of the elements present in the studied sample and, a detector. Whereas, the provides the qualitative information, the detector gives rise to the quantitative information.

III.3. XRFS vs XPS

XPS and XRFS share the same exciting beam. Nevertheless, the two X-Ray sources are different.

Briefly explain the main spectral differences that exist between these two sources and why it is necessary to have these different spectral features.

In XRFS the X-Ray source must provide the most widespread X-Ray wavelength to ensure the correct excitation of all the chemical elements present in the material, i.e. a polychromatic source. If the same polychromatic source is used in XPS, one element will provide a bunch of photo-electrons of different energies, that will complicate a lot the interpretation of the spectrum. To counteract this problem, one uses a monochromatic source which will ensure the production of only one kind of photo-electrons per analysed chemical element. This will indeed simplify the number of signals present on the XPS spectrum.

Which of these two methods is the most sensitive to the chemical nature of the neighbours of an analysed element?

According to the polychromatic nature of the X-Ray source of XRFS, most of the analysed elements lead to X-Rays resulting from the ionisation of the K level of the target chemical element. These core electrons are almost not influenced by the surrounding neighbours of the target. In contrast, due to the monochromatic nature of the X-Ray source of XPS and because the source is made of a light chemical element, one cannot always ensure the ionisation of the K level of all the chemical elements. Therefore, the target ionisation levels are most of the time the ones close or involved in chemical bounds, the energies of the target electrons being strongly dependent on the neighbourhood.

Which parameter represents the influence of the neighbourhood of an analysed element?

The chemical shift.

On a XPS spectrum, one can observe two different types of signals. How one can distinguish both?

On a XPS spectrum one can observe the signals of Auger and Photo-electrons. To distinguish both, one can change the nature of the anticathode material, so the wavelength of excitation because, the energy of the photo-electrons is linked to the energy of the exciting beam whereas, the energy of the Auger electrons is only related to the chemical nature of the emitting element.

One of these two technics must follow a correction process to achieve a good quantitative accuracy. Which technic is concerned by these so-called matrix effects? For the concerned technic, give the set of correction parameters that one must applied to meet a proper quantitative analysis.

The concerned technic is XRFS which needs a correction according to the nature of the target chemical element to access to an accurate quantitative determination.

The correction that one has to take into account are: the homogeneity of the grain of the considered material across K_G, the absorption of the emitted X-Rays as a function of the matrix K_A and the secondary fluorescence of a target element across K_F. The correction constant is then $K_m = K_G K_A K_F$. The quantitative equation using an internal standard S to obtain the relative atomic concentration of a given chemical element i is:

$$\frac{C_{ra,i}}{C_{ra,S}} = K_m \frac{I_i}{I_S} \Rightarrow C_{ra,i} = C_{ra,S} K_m \frac{I_i}{I_S}$$

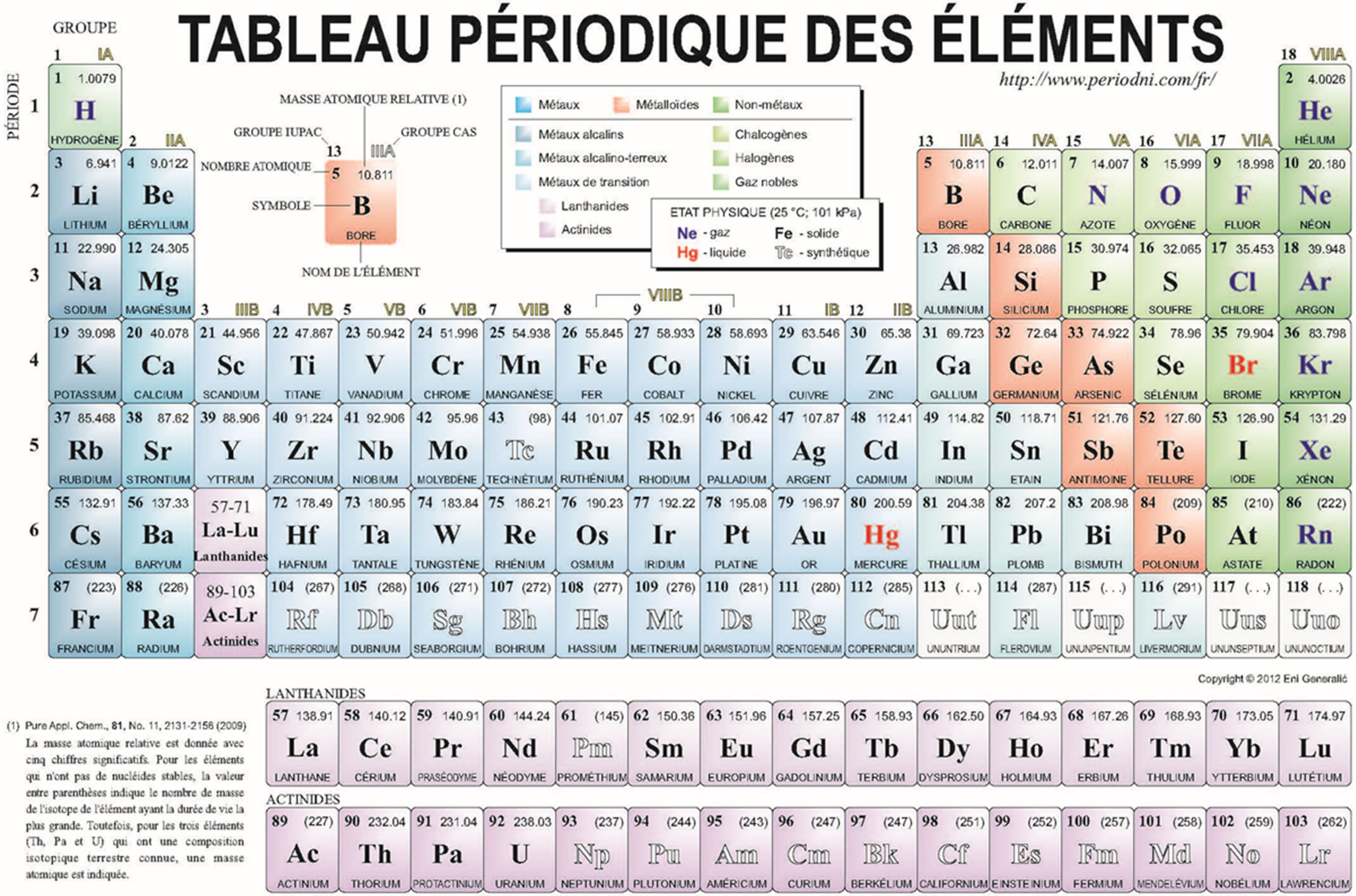


TABLEAU PÉRIODIQUE DES ÉLÉMENTS

http://www.periodni.com/fr/

- 🟦 Métaux
- 🟥 Métalloïdes
- 🟩 Non-métaux
- 🟦 Métaux alcalins
- 🟦 Métaux alcalino-terreux
- 🟦 Métaux de transition
- 🟪 Lanthanides
- 🟪 Actinides
- 🟩 Chalcogènes
- 🟩 Halogènes
- 🟩 Gaz nobles

ETAT PHYSIQUE (25 °C; 101 kPa)
Ne - gaz
Fe - solide
Hg - liquide
Tc - synthétique

PÉRIODE \ GROUPE	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 **H** HYDROGÈNE																	2 4.0026 **He** HÉLIUM
2	3 6.941 **Li** LITHIUM	4 9.0122 **Be** BÉRYLLIUM											5 10.811 **B** BORE	6 12.011 **C** CARBONE	7 14.007 **N** AZOTE	8 15.999 **O** OXYGÈNE	9 18.998 **F** FLUOR	10 20.180 **Ne** NÉON
3	11 22.990 **Na** SODIUM	12 24.305 **Mg** MAGNÉSIUM											13 26.982 **Al** ALUMINIUM	14 28.086 **Si** SILICIUM	15 30.974 **P** PHOSPHORE	16 32.065 **S** SOUFRE	17 35.453 **Cl** CHLORE	18 39.948 **Ar** ARGON
4	19 39.098 **K** POTASSIUM	20 40.078 **Ca** CALCIUM	21 44.956 **Sc** SCANDIUM	22 47.867 **Ti** TITANE	23 50.942 **V** VANADIUM	24 51.996 **Cr** CHROME	25 54.938 **Mn** MANGANÈSE	26 55.845 **Fe** FER	27 58.933 **Co** COBALT	28 58.693 **Ni** NICKEL	29 63.546 **Cu** CUIVRE	30 65.38 **Zn** ZINC	31 69.723 **Ga** GALLIUM	32 72.64 **Ge** GERMANIUM	33 74.922 **As** ARSENIC	34 78.96 **Se** SÉLÉNIUM	35 79.904 **Br** BROME	36 83.798 **Kr** KRYPTON
5	37 85.468 **Rb** RUBIDIUM	38 87.62 **Sr** STRONTIUM	39 88.906 **Y** YTTRIUM	40 91.224 **Zr** ZIRCONIUM	41 92.906 **Nb** NIOBIUM	42 95.96 **Mo** MOLYBDÈNE	43 (98) **Tc** TECHNÉTIUM	44 101.07 **Ru** RUTHÉNIUM	45 102.91 **Rh** RHODIUM	46 106.42 **Pd** PALLADIUM	47 107.87 **Ag** ARGENT	48 112.41 **Cd** CADMIUM	49 114.82 **In** INDIUM	50 118.71 **Sn** ETAIN	51 121.76 **Sb** ANTIMOINE	52 127.60 **Te** TELLURE	53 126.90 **I** IODE	54 131.29 **Xe** XÉNON
6	55 132.91 **Cs** CÉSIUM	56 137.33 **Ba** BARYUM	57-71 **La-Lu** Lanthanides	72 178.49 **Hf** HAFNIUM	73 180.95 **Ta** TANTALE	74 183.84 **W** TUNGSTÈNE	75 186.21 **Re** RHÉNIUM	76 190.23 **Os** OSMIUM	77 192.22 **Ir** IRIDIUM	78 195.08 **Pt** PLATINE	79 196.97 **Au** OR	80 200.59 **Hg** MERCURE	81 204.38 **Tl** THALLIUM	82 207.2 **Pb** PLOMB	83 208.98 **Bi** BISMUTH	84 (209) **Po** POLONIUM	85 (210) **At** ASTATE	86 (222) **Rn** RADON
7	87 (223) **Fr** FRANCIUM	88 (226) **Ra** RADIUM	89-103 **Ac-Lr** Actinides	104 (267) **Rf** RUTHERFORDIUM	105 (268) **Db** DUBNIUM	106 (271) **Sg** SEABORGIUM	107 (272) **Bh** BOHRIUM	108 (277) **Hs** HASSIUM	109 (276) **Mt** MEITNERIUM	110 (281) **Ds** DARMSTADTIUM	111 (280) **Rg** ROENTGENIUM	112 (285) **Cn** COPERNICIUM	113 (. . .) **Uut** UNUNTRIUM	114 (287) **Fl** FLEROVIUM	115 (. . .) **Uup** UNUNPENTIUM	116 (291) **Lv** LIVERMORIUM	117 (. . .) **Uus** UNUNSEPTIUM	118 (. . .) **Uuo** UNUNOCTIUM

LANTHANIDES

57 138.91 **La** LANTHANE	58 140.12 **Ce** CÉRIUM	59 140.91 **Pr** PRASÉODYME	60 144.24 **Nd** NÉODYME	61 (145) **Pm** PROMÉTHIUM	62 150.36 **Sm** SAMARIUM	63 151.96 **Eu** EUROPIUM	64 157.25 **Gd** GADOLINIUM	65 158.93 **Tb** TERBIUM	66 162.50 **Dy** DYSPROSIUM	67 164.93 **Ho** HOLMIUM	68 167.26 **Er** ERBIUM	69 168.93 **Tm** THULIUM	70 173.05 **Yb** YTTERBIUM	71 174.97 **Lu** LUTÉTIUM

ACTINIDES

89 (227) **Ac** ACTINIUM	90 232.04 **Th** THORIUM	91 231.04 **Pa** PROTACTINIUM	92 238.03 **U** URANIUM	93 (237) **Np** NEPTUNIUM	94 (244) **Pu** PLUTONIUM	95 (243) **Am** AMÉRICIUM	96 (247) **Cm** CURIUM	97 (247) **Bk** BERKÉLIUM	98 (251) **Cf** CALIFORNIUM	99 (252) **Es** EINSTEINIUM	100 (257) **Fm** FERMIUM	101 (258) **Md** MENDELÉVIUM	102 (259) **No** NOBÉLIUM	103 (262) **Lr** LAWRENCIUM

(1) Pure Appl. Chem., **81**, No. 11, 2131-2156 (2009)
La masse atomique relative est donnée avec cinq chiffres significatifs. Pour les éléments qui n'ont pas de nucléides stables, la valeur entre parenthèses indique le nombre de masse de l'isotope de l'élément ayant la durée de vie la plus grande. Toutefois, pour les trois éléments (Th, Pa et U) qui ont une composition isotopique terrestre connue, une masse atomique est indiquée.