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

Exam of Physical and Chemical Analyses of Materials

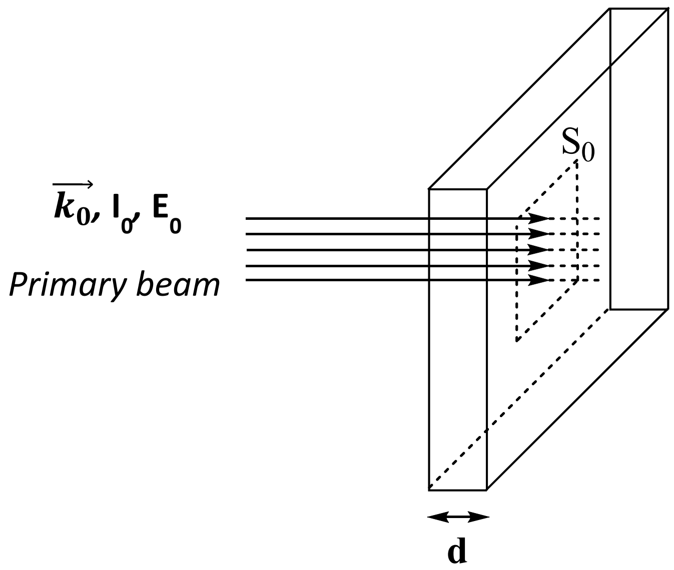
June 2024

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				
Elastic scattering				
Inelastic scattering				

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			
Compton			
Bremsstrahlung			
Diffraction			
Ionisation			

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			
Electrons			

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.

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.

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.

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

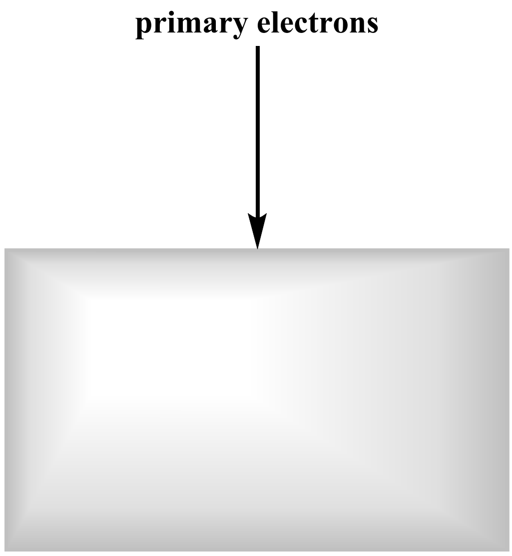
II.1. Electron microscopy

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

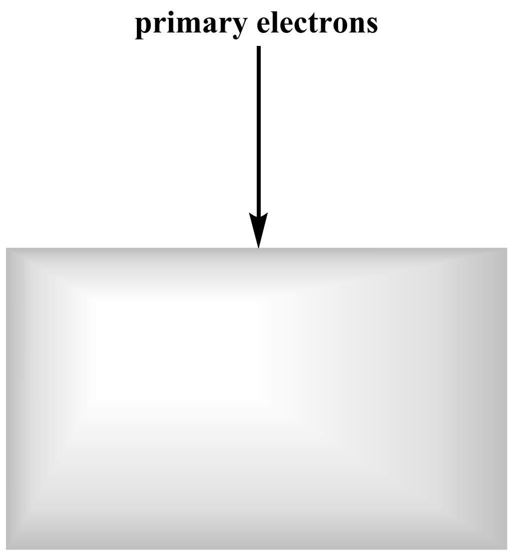
- the trajectory of the electrons in the studied sample and the specific probed sample volume

- 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		
Lateral resolution range		
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		
Type(s) of image		

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

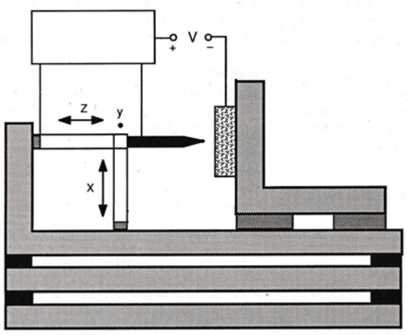
In which type of electron microscopy and for which reason(s) it may sometimes be of interest to decrease the energy of the primary electron beam?

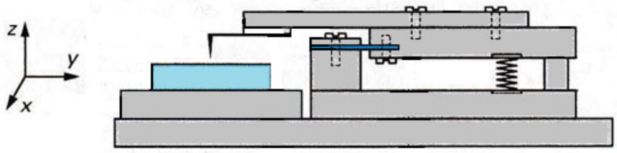
Indicate if the following statements are true or false:

	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: **B:**

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

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)?

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

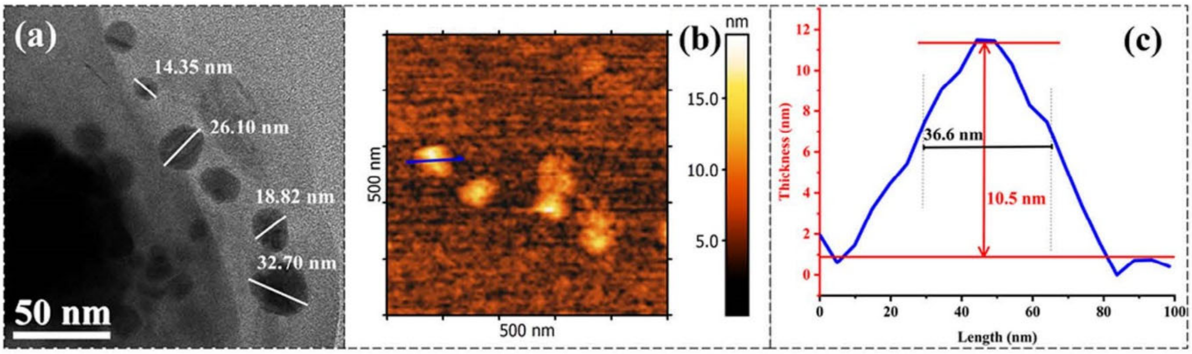
With which mode are you going to operate? Base your answer on a brief description of the chosen mode while pointing out its highlights regarding the nature of a biological membrane.

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**?

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

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

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

III. Chemical characterization of materials

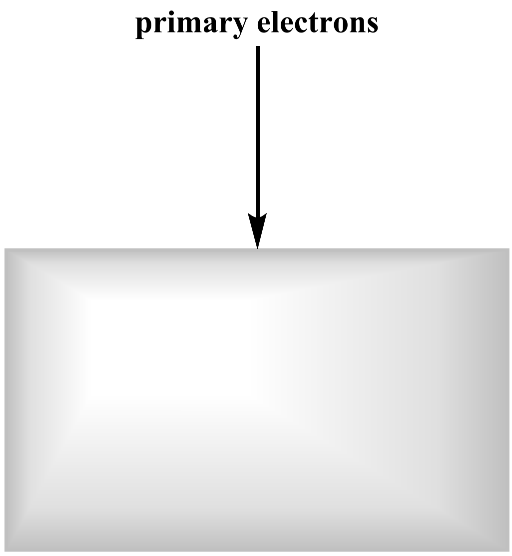
III.1. General

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

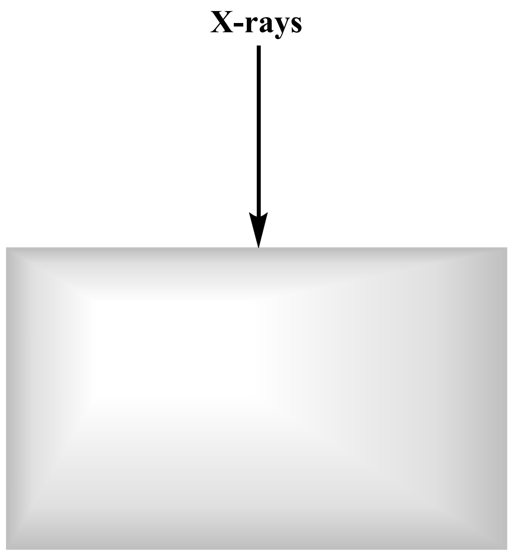
- the trajectory of the primary beam in the studied sample and the specific probed sample volume (in both cases, the primary beam does not emerge from the sample).

- 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?

III.2. Bulk and surface analyses

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

	Semi-Bulk	Bulk	Surface
XRFS			
XPS			
XRMA			
AES			

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

	X-rays as primary beam	Electrons as primary beam
XRFS		
XPS		
XRMA		
AES		

Complete the following table by filling the boxes:

	Background signal	Recorded signal	Side signal(s)
XRFS			
XPS			
XRMA			
AES			

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

Give the name of this specific apparatus.

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

Briefly describe the spectrometer associated to each apparatus?

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.

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

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

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

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.

TABLEAU PÉRIODIQUE DES ÉLÉMENTS

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

Légende : GROUPE IUPAC : 13 ; GROUPE CAS : IIIA ; NOMBRE ATOMIQUE : 5 ; MASSE ATOMIQUE RELATIVE (1) : 10.811 ; SYMBOLE : B ; NOM DE L'ÉLÉMENT : BORE

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 ; Hg - liquide ; Fe - solide ; Tc - synthétique

PÉRIODE	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	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.