INSTITUT NATIONAL DES SCIENCES APPLIQUÉES LYON

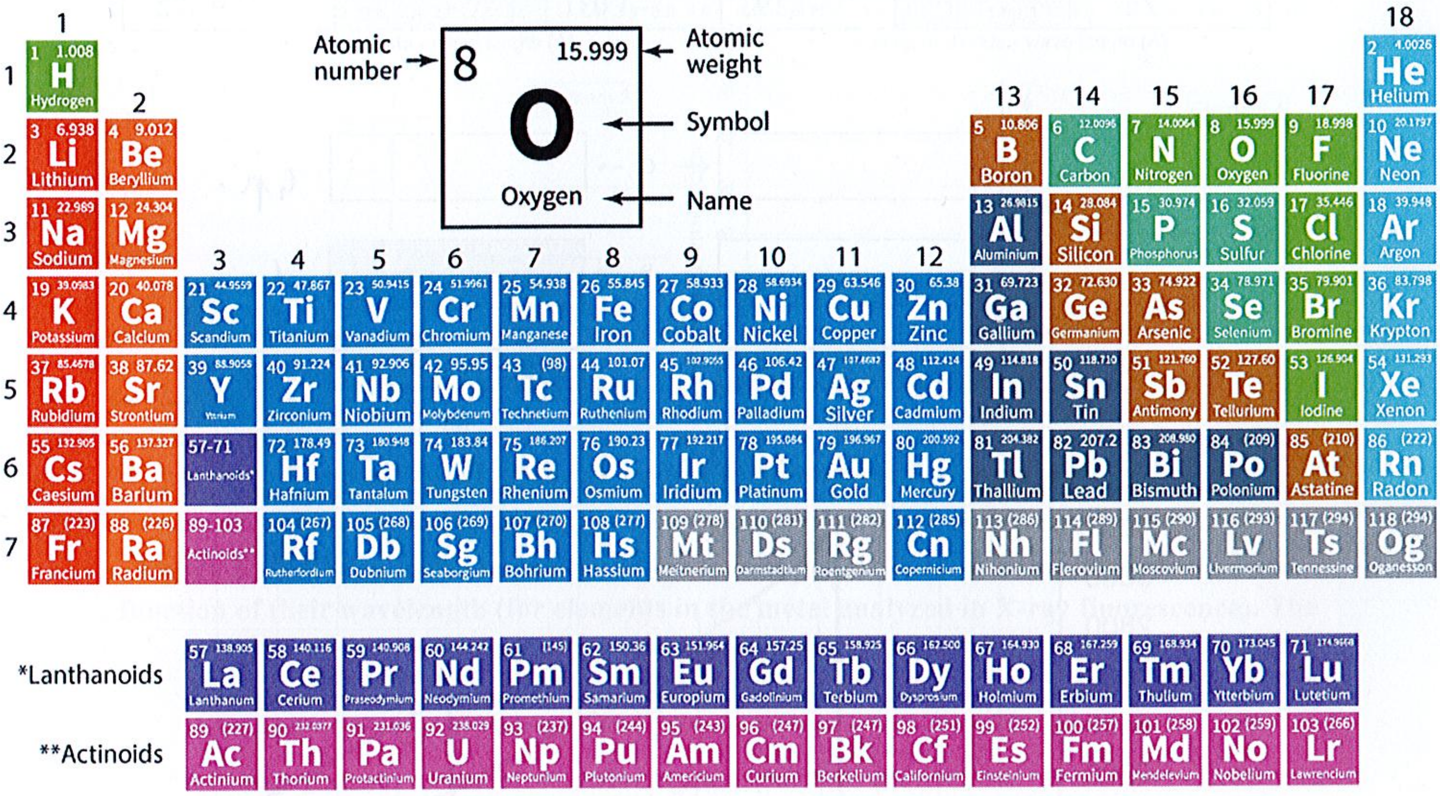
FIMI: SCAN

First Year
January 29th 2024

EC Chemistry 1 – EFS - Duration: 3 hours

Any document is prohibited. All calculators allowed.
Answers must be justified.
Indicative scale
Exercises are independent

Periodic Table of the Elements



General data:

Electronegativity (according to Pauling's scale):

$\chi_H = 2.22$ $\chi_B = 2.04$ $\chi_C = 2.55$ $\chi_N = 3.04$ $\chi_O = 3.44$ $\chi_S = 2.58$ $\chi_I = 2.66$

Planck's constant: $h = 6.626\times10^{-34}$ J.s
The Avogadro Number: $N_A = 6.023\times10^{23}$ mol^{-1}
Mass of the electron $m_e = 9.109 \times 10^{-31} kg$

Speed of light: $c = 2.998\times10^{8}$ m.s^{-1}
electron charge: $e = 1.602\times10^{-19}$ C

The relation E(eV) = 12400 / λ(Å) can be used without demonstration

Moseley's law: $\sqrt{\nu} = a(Z - b)$

Beer-Lambert's law: $I = I_0 e^{-\mu\ell}$

Selection rules for transitions between energy levels: only lines verifying:

$\Delta l = \pm 1$ and $\Delta j = 0$ or ± 1, and we will take $\Delta n \neq 0$

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Data for the X-rays problems

Table 1. Energy values in eV for the elements studied in X-ray

Elements	Level K	Level L1	Level L2,3	Transition ΔE_{KL}	Transition ΔE_{KM}
C	-284	-19	- 6		
Cr				- 5 403	- 5 944
Fe		- 846		-6 385	- 7 058
Co		- 940		- 6 922	- 7 649
Ni	- 8 332	- 1 024		- 7 455	- 8 264
Cu	- 8 992	-1 096	- 941		- 8 907
Zn		-1 193	- 1 031		- 9 572

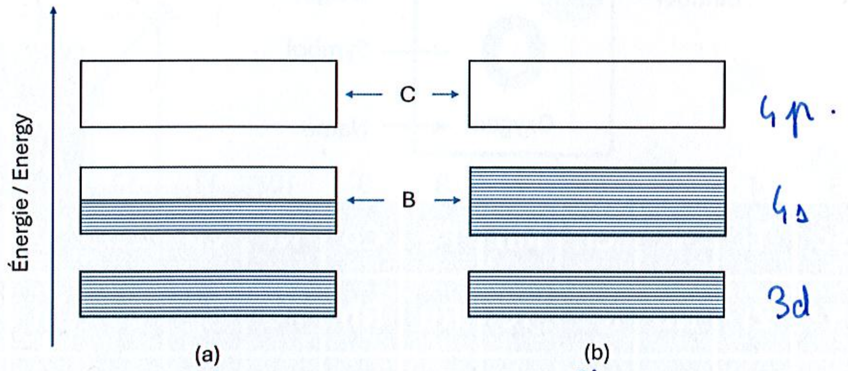


Figure 1. Representation of Energy Levels in Band Theory

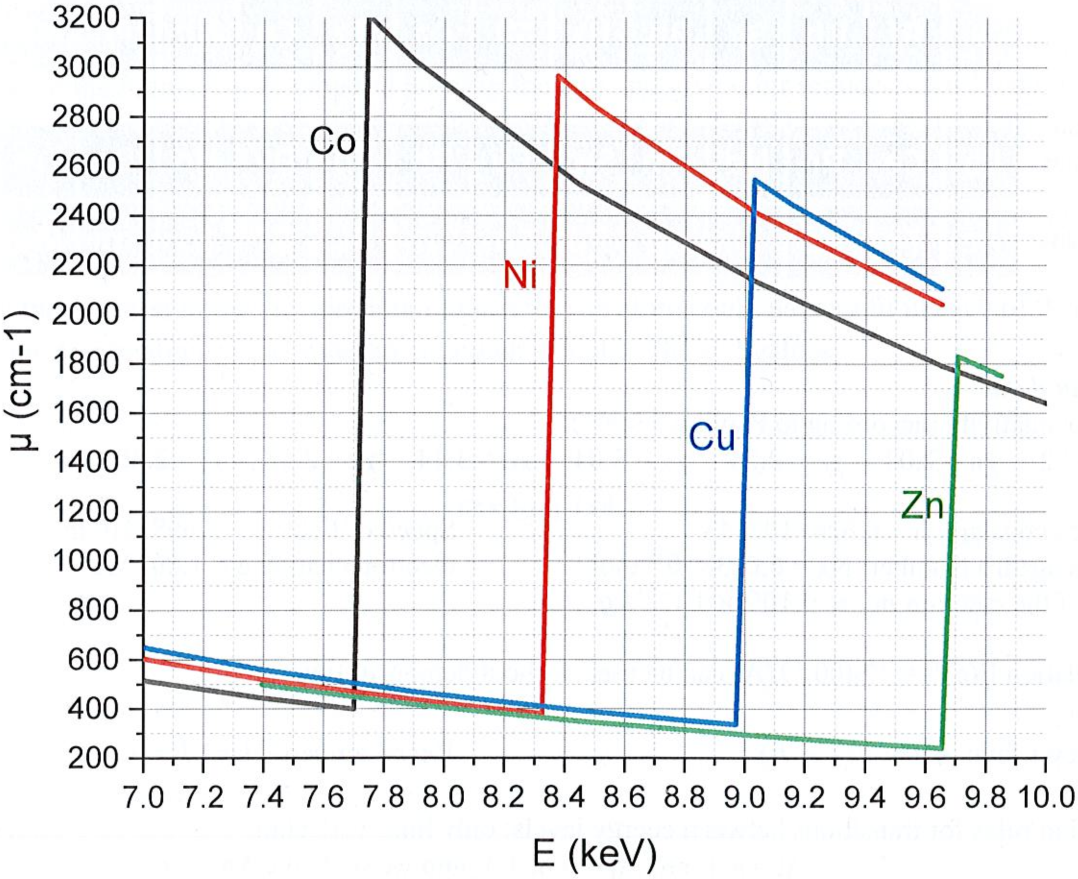


Figure 2. Evolution of attenuation coefficients as a function of energy for cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn)

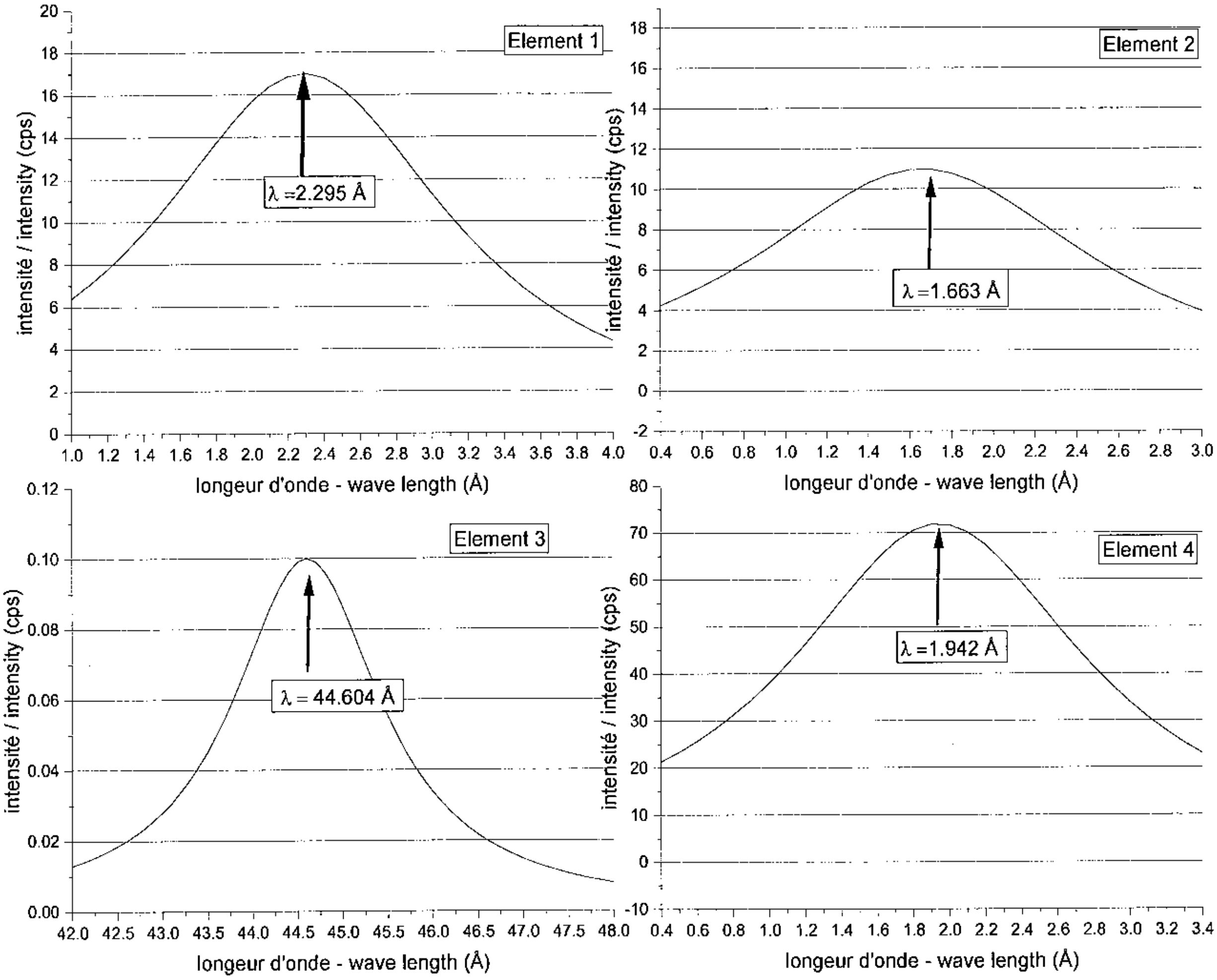
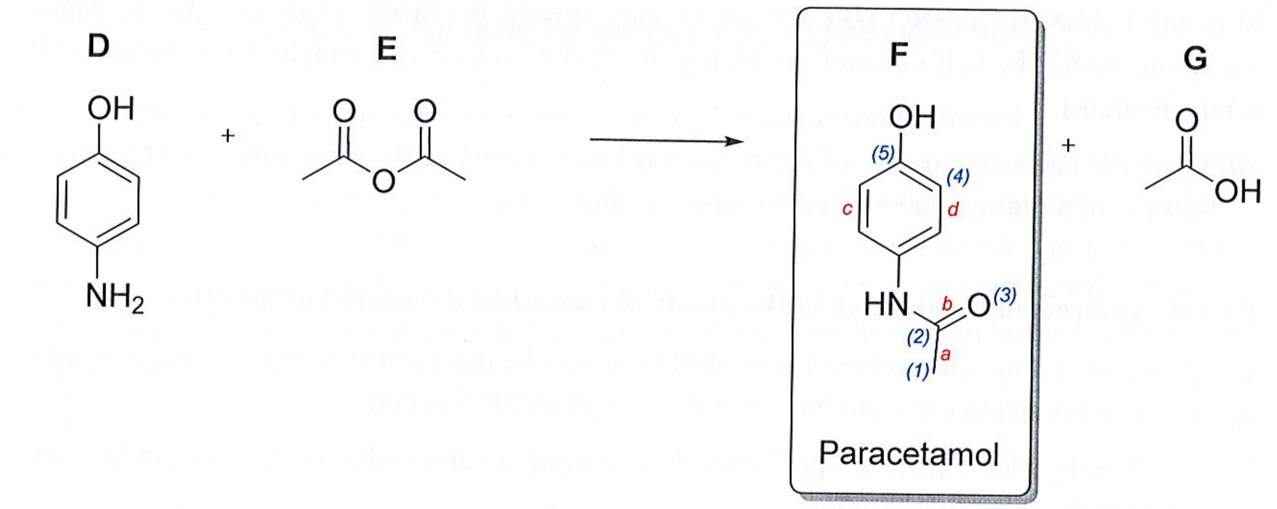


Figure 3. Evolution of the intensities in cps (count per second) of the emitted photons as a function of their wavelength (for elements in the metal analyzed in X-ray fluorescence). The accuracy of the measurements is $\lambda \pm 0.001$ Å



18) Draw the Lewis diagram of molecule **F**.

19) Determine the hybridization states of the annotated atoms (from *1* to *5*) in molecule **F**.

20) What are the orbitals involved and the associated orbital overlaps in the annotated bonds (from *a* to *d*) in molecule **F**.

21) Compare the lengths of bonds *(a)*, *(c)* and *(d)*.

Problem 2: Brass X-rays (15.25 pts)

In this part, it is proposed to use a brass (an alloy of copper (Cu) and zinc (Zn); "laiton" in French) as an anticathode in an X-ray tube in order to identify and analyze by X-ray fluorescence the chemical composition of an iron alloy.

1) Using the periodic table, write down the electronic structure of zinc and copper.

2) For zinc, give the values of the quantum numbers (n, m_ℓ, ℓ, j, s) of its valence shell electrons. Name the energy level(s) involved.

3) Discuss the nature and strength of the bonds between copper and zinc atoms in brass. Give two physical properties associated with this type of bonding.

4) From the diagram represented in *Figure 1*, specify what the annotated bands B and C correspond to. Which physical property accompanies each of the two cases presented in (a) and (b) of *Figure 1*?

5) What is the minimum voltage that must be applied to the X-ray tube to produce all the emission lines of the brass? Justify your answer.

6) The incident electrons given by the filament arrive on the brass anticathode at a velocity of 1.027×10^{8} m.s^{-1}. Calculate the voltage that was applied to the X-ray tube (you will neglect the initial velocity of the electrons and the correction of relativity).

7) Calculate the limit wavelength of the continuous background for this voltage.

8) Compute the energy (to within 1 eV) of the photons emitted by the brass anticathode (the ones involving K level) and their corresponding wavelengths (to within 10^{-2}Å).

9) In the $C_6H_5NO_3/C_6H_7NO$ (**B/D**) redox couple, specify the atom(s) that change the degree of oxidation. Write the half-equation involving the $C_6H_5NO_3/C_6H_7NO$ couple (to be balanced in an acidic medium).

10) Write the balance equation of the redox reaction between ($\underline{B}H_4^-$) and molecule **B**. Specify the number of moles of electrons exchanged per mole of **B**.

Part B - Indirect determination of the purity of commercial sodium borohydride

The purity of commercial sodium borohydride needs to be determined prior to its use as a reducing agent. It is proposed to carry out this control by a volumetric titration.

Initially, borohydride ions react quantitatively in a basic medium with an excess of iodate ion IO_3^- according to the following reaction:

$4\,IO_3^- + 3\,BH_4^- \rightleftharpoons 4\,I^- + 3\,OB(OH)_2^- + 3\,H_2O$ *(Reaction 1)*

To measure the excess iodate ions, they are then reacted in an acidic medium with an excess of the iodide ion I^- *(Reaction 2);* the iodine formed I_2 is then measured by the thiosulfate ions $S_2O_3^{2-}$*(Reaction 3*).

11) Give Lewis' formulas of $\underline{I}O_3^-$ and $O\underline{B}(OH)_2^-$

12) Using the oxidation numbers, write down the half-reaction involving the iodine atoms in *reaction 1*. Similarly, using the oxidation numbers, identify and give the half-reaction of the other redox couple participating in *Reaction 1*.

13) Concerning the $\underline{I}O_3^-/I_2$ and I_2/I^- couples,

a) Write down the two half-equations involved (to be balanced in an acidic medium) using the oxidation degrees.

c) Write the balance equation of *Reaction 2* (involving IO_3^-/I_2 and I_2/I^- couples).

14) Regarding the sulfur element:

a) To which period and group does element S belong to?

b) Compare its first ionization energy with the one of oxygen.

c) What ion does sulfur tend to form?

15) Write down the Lewis formulae for the following sulfur containing compounds: $\underline{S}O_3^{2-}$, $S_2O_3^{2-}$ *(the central S atom is connected to the other S atom and the O atoms)*, $S_4O_6^{2-}$ *(the S atoms form a linear chain and the O atoms are symmetrically distributed at both ends of the chain).* Determine the oxidation number of each of the sulfur atoms for these three ions.

16) Briefly explain if there are any mesomeric formulas for $\underline{S}O_3^{2-}$ and give the resonance hybrid. Represent its geometry according to the VSEPR rule, specifying the value of the angles.

17) Write the half-equation involving the couple $S_4O_6^{2-}$ / $S_2O_3^{2-}$ and then write the balance equation (*Reaction 3*).

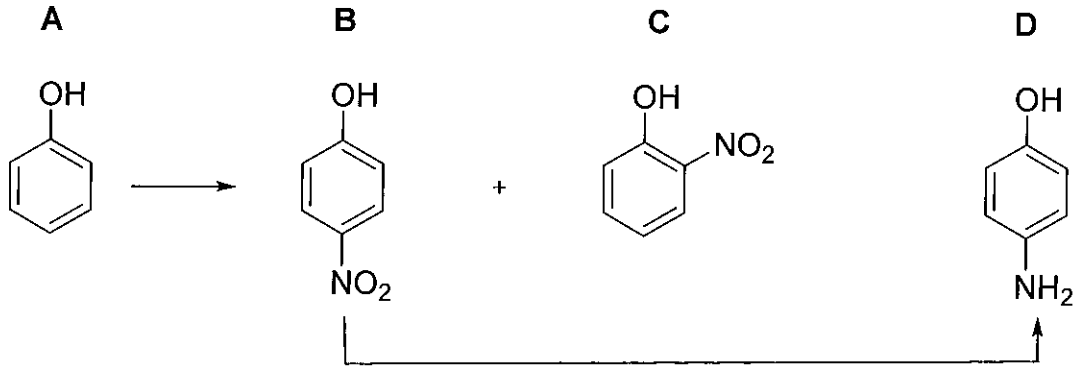
Part C - Synthesis of the pain killer paracetamol

Para-aminophenol C_6H_7NO (molecule **D)** reacts with acetic anhydride $C_4H_6O_3$ (molecule **E**) to form paracetamol $C_8H_9NO_2$ (molecule **F**) and acetic acid $C_2H_4O_2$ (molecule **G)**

Problem 1: Synthesis of paracetamol from phenol (22 pts)

Part A - Synthesis of the precursor 4-aminophenol (or para-aminophenol)

The synthesis of para-aminophenol (molecule D) from phenol (C_6H_6O, molecule **A**) takes place in two steps. The first step is a nitration of phenol (molecule **A**). For this, a mixture of sulfuric acid (H_2SO_4) and nitric acid ($HO\underline{N}O_2$) is used. Under these conditions, nitric acid forms the nitronium ion ($\underline{N}O_2^+$) which replaces one hydrogen atom of phenol. There are two possible reaction sites on the phenol molecule and the nitration reaction leads simultaneously to 4-nitrophenol (molecule **B**) and 2-nitrophenol (molecule **C**).



1) Represent the Lewis formula for the phenol molecule (**A**). Which atoms are coplanar (justify your answer)?

2) By losing the proton of the alcohol function (-OH), phenol (C_6H_6OH) becomes the phenolate anion ($C_6H_5O^-$). Write the complete Lewis structure of the phenolate ion ($C_6H_5O^-$). Suggest three possible mesomeric formulas that possess a negative charge on carbon atoms of the benzene ring (ring composed of carbon atoms).

3) Write Lewis' formulas for nitric acid ($HO\underline{N}O_2$) and nitronium ion ($\underline{N}O_2^+$) (the underlined atom is the central atom). Specify if there are mesomeric formulas for these two compounds. For the nitronium ion ($\underline{N}O_2^+$), give its VSEPR formula and represent it by specifying the value of the angles around the underlined atom.

4) If justified, indicate whether the two species $HO\underline{N}O_2$ and $\underline{N}O_2^+$ form a redox couple. If yes, write the redox pair as ox/red.

5) Draw the Lewis structure of molecule **C**.

6) Assign the following melting temperatures of 43°C and 113°C to compounds **B** or **C**, with justification.

4-nitrophenol $C_6H_5NO_3$ (molecule **B**) is then used. When reacting with the borohydride ion (BH_4^-), it forms para-aminophenol C_6H_7NO (molecule **D**).

7) Write the Lewis structure of the borohydride ion ($\underline{B}H_4^-$). Represent its geometry according to VSEPR by specifying the value of the angles around the central atom (underlined).

8) Knowing that the borohydride ion acts as a reducer, indicate in the following half-equation which atom(s) change their oxidation number by giving their corresponding oxidation numbers. Identify the oxidized form and the reduced form.

$$BH_4^- \rightleftharpoons BH_3 + 2e^- + H^+$$

9) Initially, on the X-ray tube's window a metal filter is applied. By exploiting the *Figure 2*, indicate whether each of the proposed filters can be used to attenuate the KL emission lines of brass. Justify your answer.

10) What is the thickness of the copper filter (in μm) that would attenuate 95% of the shortest wavelength KL's line emitted by brass?

In X-ray fluorescence analyzers, it is imperative to work with a monochromatic beam (with a single wavelength) at the exit of the ray tube to ensure the quality and accuracy of the results. The use of a brass anticathode makes this task complex due to the presence of several KL and KM lines at the exit of the tube. This makes it necessary to correctly select a filter at the outlet of the tube.

11) Using *Figure 2*, provide a schematic diagram showing which filter(s) would monochromatize the beam.

12) Monochromatization of the beam is achieved with a 10 μm thick nickel (Ni) filter. To be considered satisfactory, the following two conditions must be met: the attenuation of the line of interest must be less than 40%, and the ratio of the emitted intensities must be greater than 50. Knowing that the incident intensity ratio $\frac{I_{KL}^0}{I_{KM}^0}$ = 10.0, verify conditions and justify your answer. The μ values to be considered are either 410 cm^{-1} or 2125 cm^{-1}.

13) The analysis of an X-ray fluorescence metal alloy in wavelength dispersion provides the four diagrams shown in the *Figure 3*. Identify the elements being analyzed with the help of the *Table 1*. Give the mass percentage composition of the alloy assuming that the intensity of the measured peaks (in cps) is equal to the mass percentage of the element being analyzed.

Problem 3: Crystallography (22.75 pts)

Copper (Cu) crystallizes in a face centered cubic structure with a lattice parameter of a= 3.610Å. It has a density of 8.96 $g.cm^{-3}$.

1) Determine the number of motif(s) per cell of such structure.
2) What is the composition of the motif? Justify.
3) What is the coordination number of a copper atom in this structure?
4) Calculate the metallic radius of copper (justify your calculation).
5) Calculate the atom packing factor (APF) of the structure. What can we say about this APF value?

Brass α is an alloy of copper and zinc. Its structure is comparable to the previous copper structure but the atoms located in the center of the faces are substituted by zinc atoms. The cubic cell parameter then becomes a_α=3.696 Å and the density is 8.44 $g.cm^{-3}$

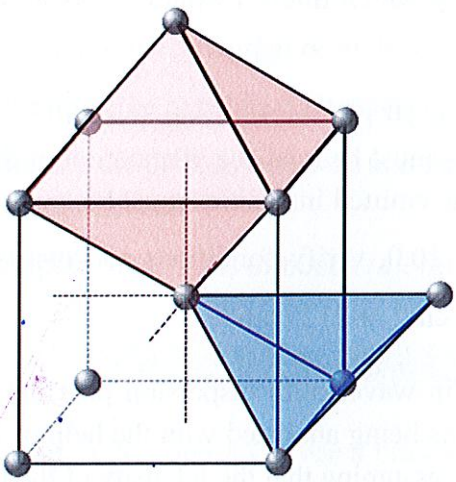
6) Represent the crystalline lattice showing the position of the copper and zinc atoms.
7) What is the formula of the alloy in the form Cu_xZn_y.
8) Calculate the radius of the zinc atom assuming that the radius of copper is unchanged.
9) Calculate the APF of this material.

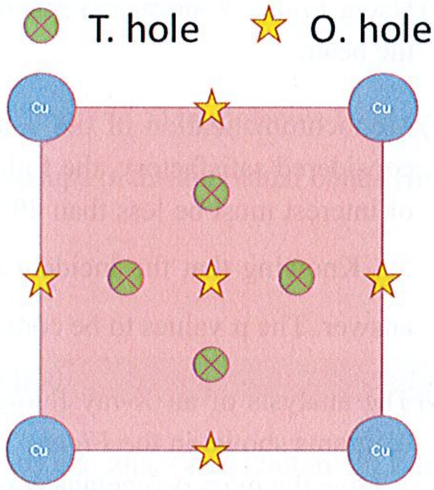
We now consider a brass β with a density of 7.796 $g.cm^{-3}$ and corresponding to the formula CuZn where copper occupies the vertices of a cube and Zn lies at the center of the cube

10) What is the motif in this structure? Give its cell lattice.

11) What is the parameter a_β of this new structure.

The following diagrams show a 3D representation and face of the β cubic structure. The positions of the center of the interstitial holes (tetrahedral – circles - and octahedral – stars - holes) are shown on the second scheme. Please note that in this type of structure the volumes of tetrahedral and octahedral holes can overlap.





12) Calculate the number of octahedral holes in the cell and give their reduced coordinates.

13) Calculate the number of tetrahedral holes in the cell and give their reduced coordinates.

14) For the octahedral hole, give the 2 possible distances between the center of the hole and one of its vertices as a function of the parameter a_β.

15) For the tetrahedral hole, give the distance between the center of the hole and one of its vertices as a function of the parameter a_β.

16) Give the expression for the maximum radius that an atom could have to fit in each of these holes without deformation of the structure and then calculate these 2 values.

*** End ***