EC Chemistry 1: Architecture of matter – IE n°2 - Duration : 2h

No documents allowed.
All non-connected calculators without AI allowed.

Results will be given with the appropriate significant numbers.
Please return, the appendix with your copy

Usual constants : $h \approx 6.626 \times 10^{-34}$ J.s ; $c \approx 2.998 \times 10^{8}$ m.s^{-1} ; $e \approx 1.602 \times 10^{-19}$C ;
$m_{e^-} \approx 9.109 \times 10^{-31}$Kg
Beer-Lambert's law : $I = I_0 \exp(-\mu.x)$ with μ the linear absorption coefficient et x the thickness
Moseley's law : $\sqrt{\nu} = a.(Z - b)$
Selection rules : $\Delta l = \pm 1$ et $\Delta j = 0$ or ± 1
Relationship between E and λ : $E(eV) = 12400/\lambda\,(\text{Å})$

Elements	**H**	**C**	**N**	**O**	**S**	**Cl**	**Fe**	**I**
Z	1	6	7	8	16	17	26	53
$\chi(Pauling)$	2.1	2.5	3.0	3.5	2.5	3.0	1.8	2.5

Part I – Bonding

1 Briefly explain the difference between a dative (or coordinative) bond and a typical covalent bond.

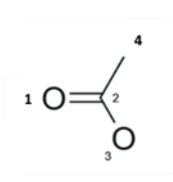
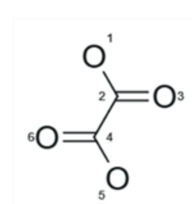
Consider the following molecules: HCl, H**N**O$_3$, H$_2$**S**O$_4$, H$_2$O$_2$. Knowing that the underline atoms are the central ones and that the hydrogen atoms are only linked to oxygen atoms in H**N**O$_3$, H$_2$**S**O$_4$, H$_2$O$_2$.

2 Write down the most representative (probable) Lewis formula for these molecules. Justify your answer by illustrating the (possible) formal charges.
If any, write down the mesomeric forms and represent the corresponding resonance hybrid.

3 For each compound, indicate the type of geometry according to Gillespie's model and draw the geometric shapes deduced from VSEPR theory. Indicate the value of the bond angles around the central atom or one atom of O in H_2O_2.

4 Determine and justify whether these molecules possess a permanent dipole moment.

Acetic acid $C_2H_4O_2$ and oxalic acid $C_2H_2O_4$ have the following structures (all H atoms were removed):

Acetic acid	Oxalic acid
	

5 Reproduce these two structures, showing all the atoms and all the non-bonding doublets.

6 Determine and justify the hybridization states of the carbon and oxygen atoms for these two molecules. Describe the nature of the bonds between the carbon C_2 and oxygen O_1 in these two molecules, based on the atomic orbitals involved.

7 Identify and justify the non-coplanar atoms in acetic acid. On a new diagram, represent the nonhybridized orbitals (fragments) for this acid.

Part II – X-rays and spectroscopy

Table 1. Energy data for various elements of the periodic table.
Only K-L et K-M transitions are considered.

Elements	$^{51}_{23}\mathbf{V}$	$^{52}_{24}\mathbf{Cr}$	$^{55}_{25}\mathbf{Mn}$	$^{56}_{26}\mathbf{Fe}$	$^{59}_{27}\mathbf{Co}$	$^{58}_{28}\mathbf{Ni}$	$^{63}_{29}\mathbf{Cu}$	$^{64}_{30}\mathbf{Zn}$	$^{96}_{42}\mathbf{Mo}$	$^{103}_{45}\mathbf{Rh}$
$\mathbf{E_K}$ (KeV)	-5.47	-5.99	-6.54	-7.11	-7.71	-8.33	-8.98	-9.66	20.00	-23,22
$\mathbf{\Delta E_{K-L_{2,3}}}$(KeV)	-4.95		-5.90	-6.41	-6.93	-7.48	-8.05		-17.48	-20,22
$\mathbf{\Delta E_{K-M_{2,3}}}$(KeV)	-5.43		-6.49	-7.06	-7.65	-8.27	-8.90		-19.61	-22,72

Figure 2 in the appendix shows a schematic diagram of an X-ray tube used for an X-ray fluorescence analysis of a target sample.

1 Complete the *Figure 2* in appendix by identifying the essential elements and represent, by identifying, the various discrete X-rays involved.

2 Explain the physical phenomena associated with the record of a continuous background and discrete lines associated with the production of X-rays on an emission spectrum.

3 For a copper anticathode, plot the emission profile spectum ($I = f(\lambda)$) on *Figure 3* of the appendix. Consider the acceleration voltages : $U_a = 5$ kV ; 8,5 kV ;10 kV et 40 kV. Justify the chages in emission spectra and discret lines.

4 For an acceleration using a voltage of $U_a = 40\mathrm{kV}$, determine the maximum speed of the incidence electrons when they strike the copper anticathode (neglect the electrons' initial speed and the relativity correction). Calculate the limiting wavelength of the continuous background.

5 Complete the energy diagram for copper in the appendix *Figure 4*, specifying the quantum number (n, l, j) corresponding to each energy level involved. Identify and justify the characteristic emission lines involving the K energy level only.

We are now working on the monochromatization of the Coppe X-ray tube

6 Among the elements in Table 1, which ones can be used as a filter to monochromatize the X-rays produced by the Coppe tube?

7 The copper anticathode emits X-rays with intensity for $K - L_{2,3}$ lines 5.7 times greater than that of $K - M_{2,3}$. Linear attenuation coefficients characterize the chosen filter:
$\mu_{K\text{-}L2,3} = 432.7\ cm^{-1}$ and $\mu_{K\text{-}M2,3} = 2488.7 cm^{-1}$.

To ensure monochromatization, we assume that the intensity of the $K - L_{2,3}$ radiation passing through this filter must be at least 95%.
What is the minimum thickness necessary for the filter?

Once monochromatized, the X-rays are sent to a target sample for X-ray fluorescence analysis.

8 Describe photoelectric and diffusion phenomena. Specify which one of these two phenomena is responsible for fluorescence.

9 Explain why the energy of the monochromatic $KL_{2,3}$.beam from the Copper X-ray tube is not sufficient to cause the K fluorescence of the element molybdenum (Mo).

10 Using Table 1, suggest another element to act as an anticathode to induce such fluorescence. Justify your answer.

The X-ray tube selected for this exercise can analyze elements up to Molybdenum (Mo). An alloy is analyzed by X-ray fluorescence and the spectrum (simplified for the exercise) is given below (*Figure 1*).

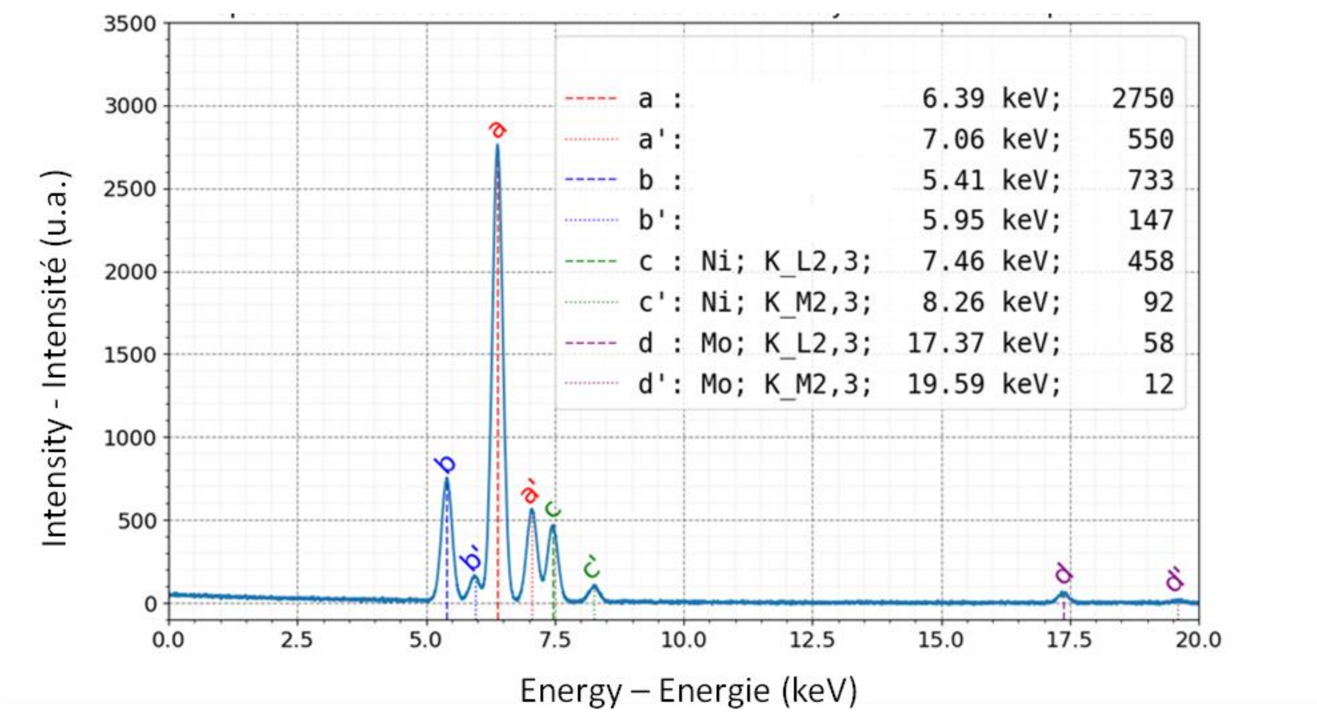


Figure 1. Intensity vs Energy spectrum for an alloys analyzed by X-ray fluorescence.

The peaks noted [a, a', b, b'] are derived from the various elements listed in *Table 1*.

11 Calculate the missing data in *Table 1* and explain your approach.

12 Identify the elements and transitions associated with the peaks noted [a, a', b, b'].

***Part III* – Redox**

1 Justifying by calculating the oxidation numbers, indicate whether or not the proposition below could be redox couples. If so, specify the oxidized form, then the reduced form and the corresponding redox half-equations in acidic solution:

H_2O and O_2 (1)

Fe and Fe^{2+} (2)

IO_3^- and I_2 (3)

Fe^{3+} and $[FeCl_4]^-$ (4)

2 Write down the global equation related to the $Cr_2O_{3(s)}$ oxidation to $Cr_2O_{7(aq)}^{2-}$ by the redox couple ClO_2/Cl^-in basic solution. Justify your approach and specify the number of moles of electrons exchanged per mole of oxydant.

3 Calculate the oxidation numbers of the different carbon atoms in the acetic acid molecule (formula given in Exercise 1). Justify your answer.

*** End ***

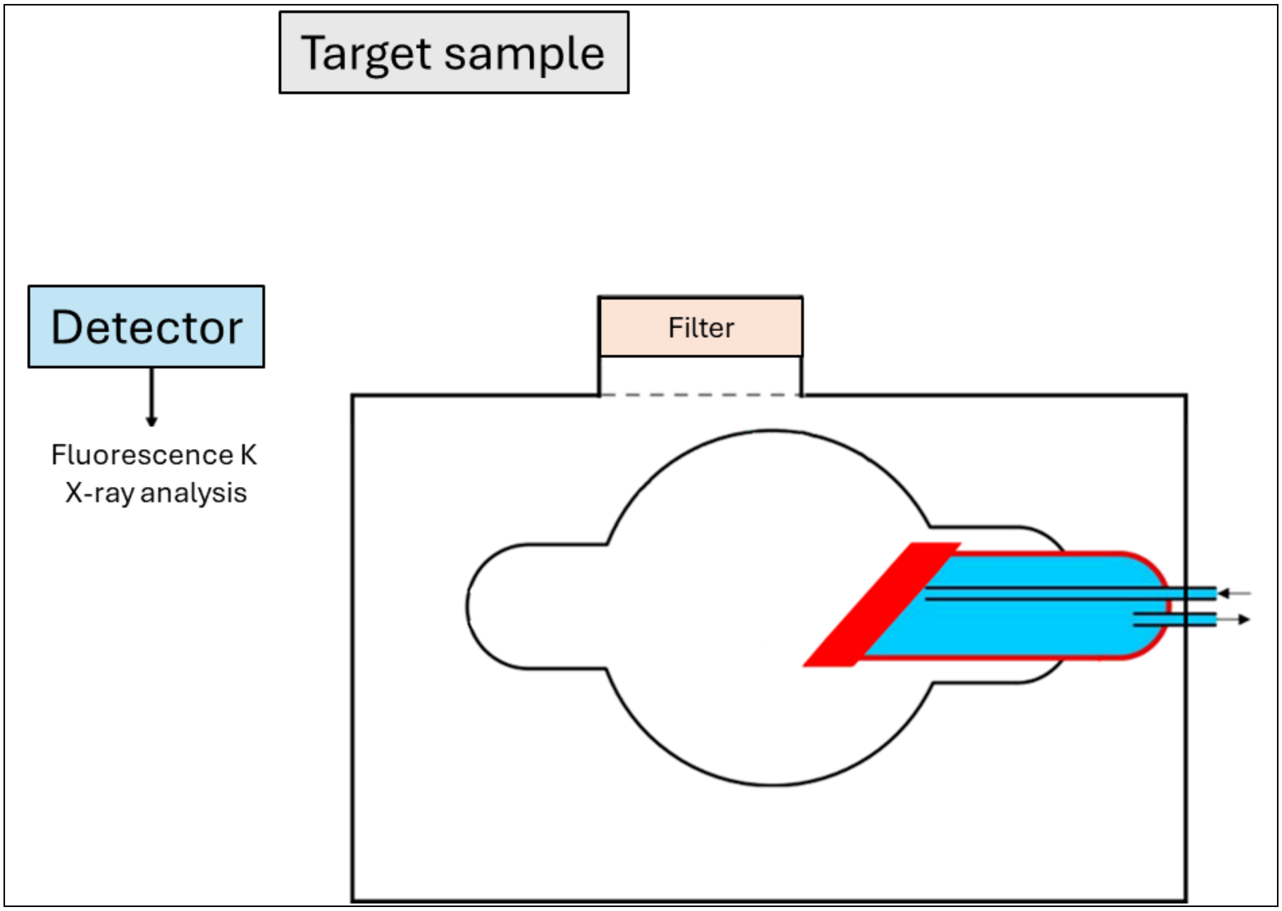


Figure 2 **: Schematic diagram of X-ray fluorescence elemental analysis**

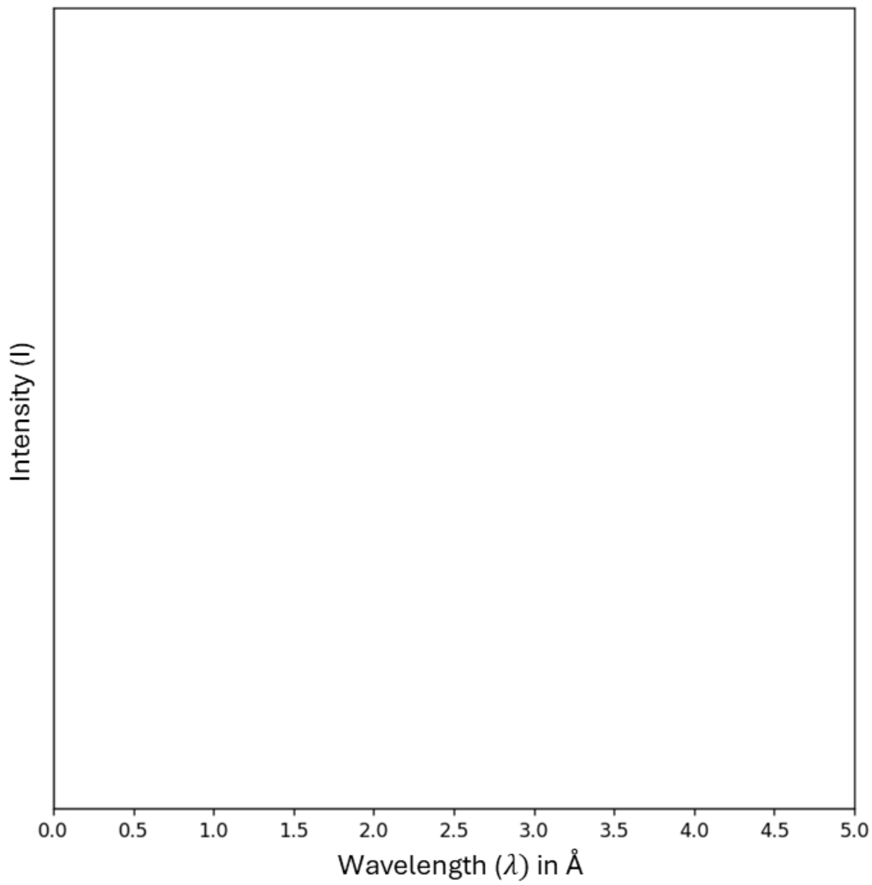


Figure 3 **: X-ray emission spectrum from copper X-ray tube as a function of acceleration voltage**

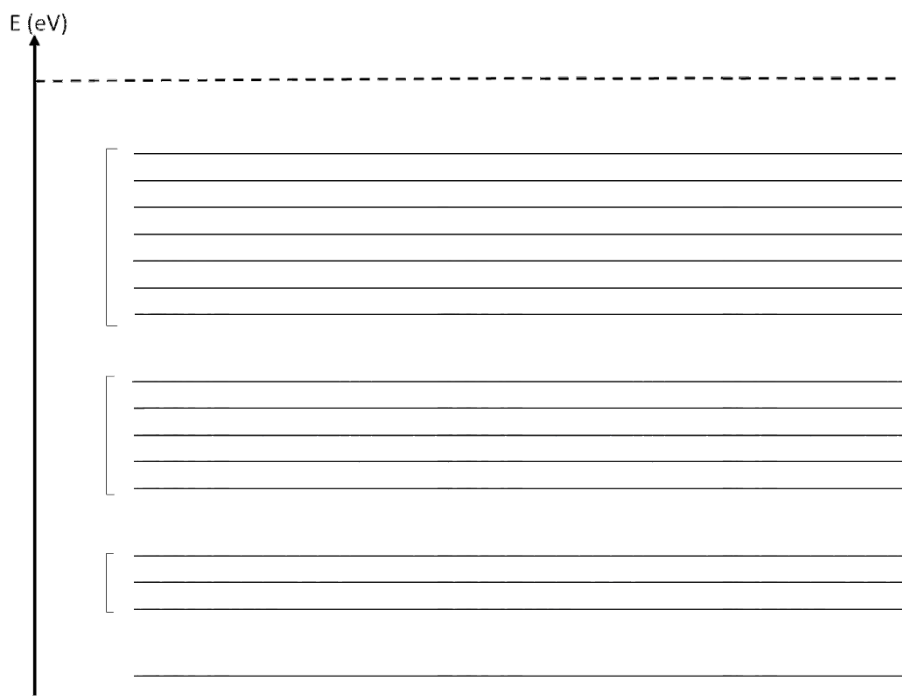


Figure 4 **: Diagram of electron energy levels of copper atom permitted in X-ray photon emission**