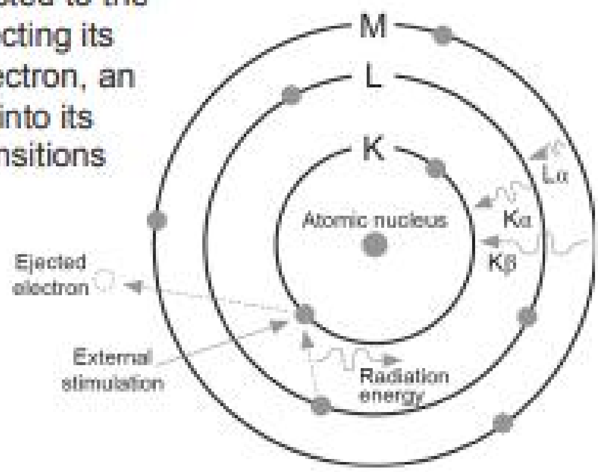
Question 22 **(20 marks)**

X-ray fluorescence (XRF) analysis and application

Art forgery is the creating and selling of works of art which are credited falsely to other artists. Modern dating and analysis techniques have made the identification of forged artwork much easier.

X-ray fluorescence is the emission of characteristic X-rays having specific photon energies from a material that has been excited. This is widely used for chemical analysis, such as in determining the materials used in paintings.

In order to excite an atom to produce an X-ray that is unique to that element, external stimulation in the form of high-energy particles or X-rays removes an inner K shell electron. The X-ray source uses a known element and bombards it with accelerated electrons as a form of external stimulation. As an electron in the atom falls back to replace the removed electron, it produces an X-ray of a known energy. This specific X-ray is then directed to the unknown material, providing external stimulation and ejecting its innermost electron. Following the ejection of an inner electron, an electron from the unknown element's outer shells drops into its place producing unique energy transitions. The main transitions are given names:



- L→K transition is traditionally called $K\alpha$,
- M→K transition is called $K\beta$,
- M→L transition is called $L\alpha$, and so on.

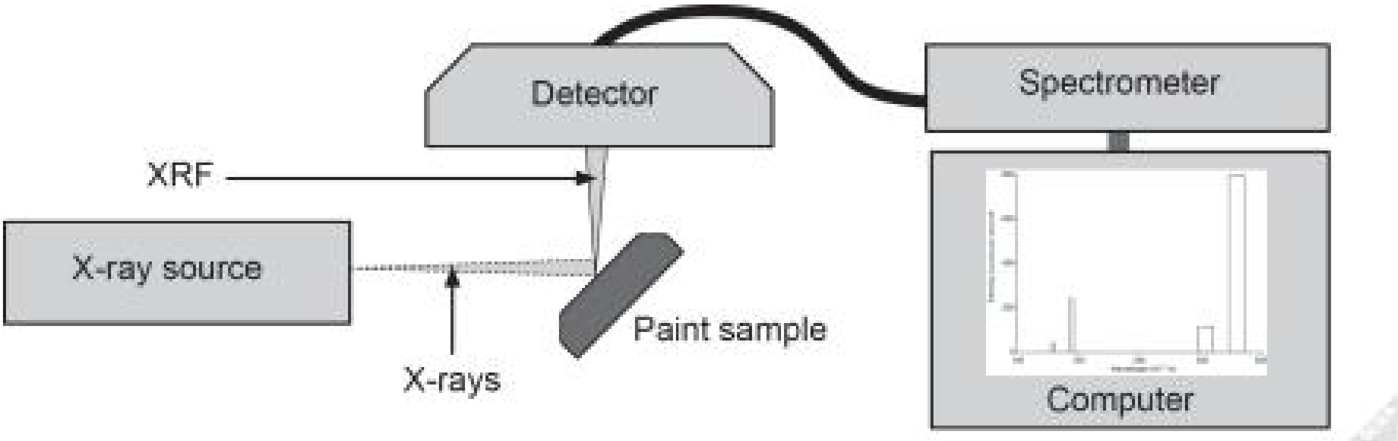
Each of these transitions yields a fluorescent photon which can be detected and analysed. Once sorted, the intensity of each characteristic radiation is related directly to the amount of each element in the material.

Atomic number	Element	Symbol	$K\alpha$ energy (keV)	$K\beta$ energy (keV)
22	titanium	Ti	4.511	4.931
30	zinc	Zn	8.639	9.572
45	rhodium	Rh	20.216	22.724
50	tin	Sn	25.271	28.486

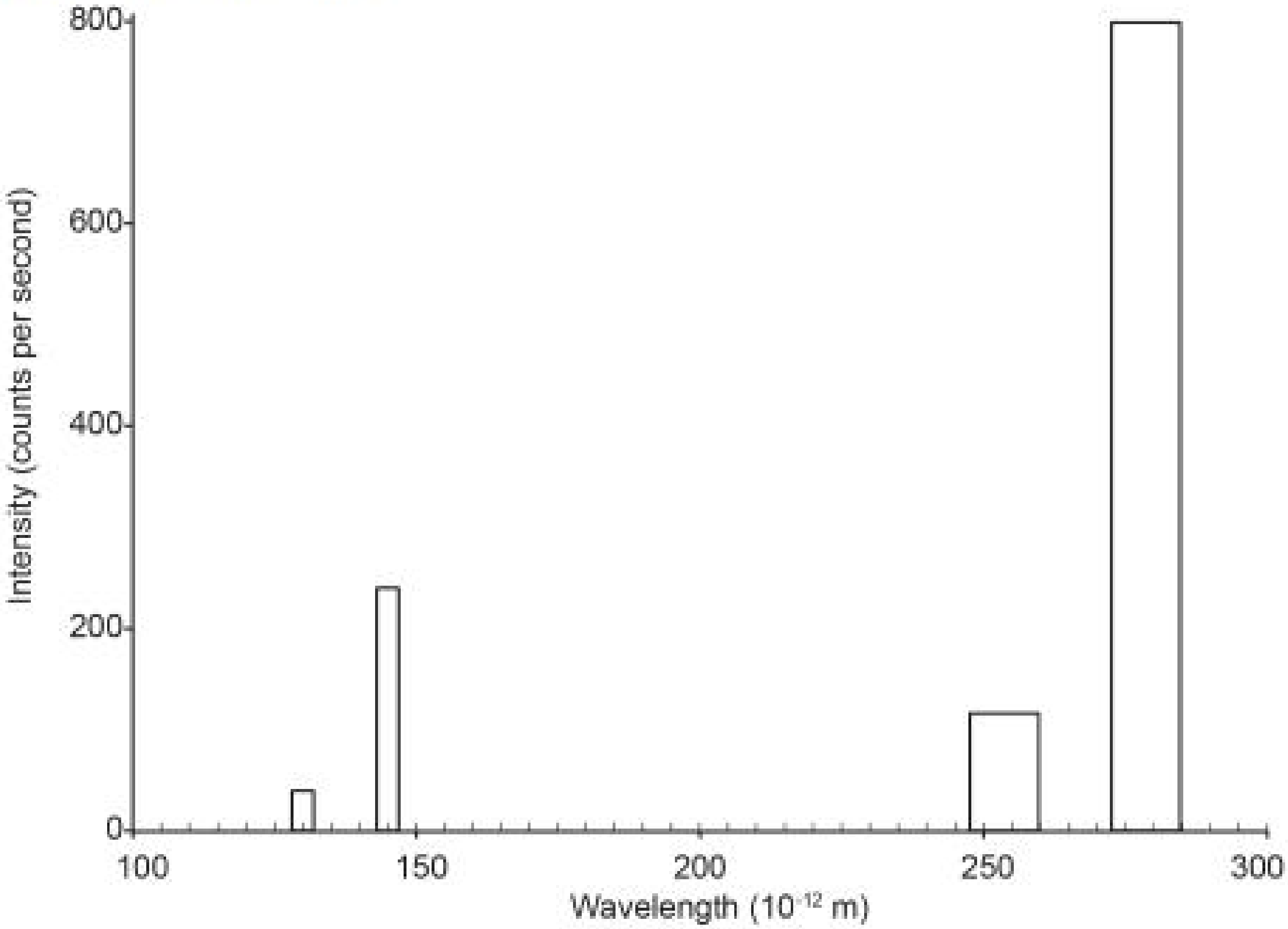
Table 1: Characteristic $K\alpha$ and $K\beta$ fluorescent X-ray energies for various elements.

The most straightforward and frequent application of XRF in the art industry is to determine the elements that make different paint colours. The question of whether a particular painting is a forgery or an authentic one, can be determined if the presence of a particular paint provides evidence for the age of the painted area. For example, titanium white (titanium dioxide, TiO_2) has only been available since about 1920 as a replacement for zinc white (zinc oxide, ZnO) which was widely used from 1850 until it was replaced around 1920.

A painting offered for sale recently was claimed to be painted in about 1890. An XRF elemental mapping was carried out on the white areas of the suspect painting. The analysis was performed as shown in the diagram on page 33.



The incident X-ray beam consisted of the Kα emission from rhodium in the X-ray source. The XRF results are shown below.



The resultant X-ray fluorescence spectrum

(a) The rhodium is bombarded with high energy electrons to produce the Kα photons. The energy required to remove the electron from the K shell is greater than the Kα energy. Explain where the extra energy goes. (2 marks)

(b) Consider the XRF spectrum on page 33. Kα produces one of the peaks at 130×10^{-12} m and 145×10^{-12} m, while Kβ produces the other. Which emission, Kα or Kβ, is more likely to occur? Explain your answer. (3 marks)

(c) The equipment set up as discussed in the article is used to detect titanium.

(i) Explain why it would **not** be possible to detect the Kα fluorescent X-ray from tin. (2 marks)

(ii) The electrons that bombard rhodium in the X-ray source have an energy of 60.0 keV. If one of these incident electrons caused an electron to be ejected from the K shell of a rhodium atom, calculate the maximum speed of the ejected electron. Ignore any relativistic effects. (4 marks)

(d) Looking at the resultant XRF spectrum, is there any evidence of titanium dioxide present in the painting? Justify your answer. (6 marks)

(e) Is the painting a forgery? Explain your reasoning. (3 marks)