ANALYSIS OF AN ANCIENT ARTEFACT OF VI-VII CENTURY AD WITH X-RAY FLUORESCENCE

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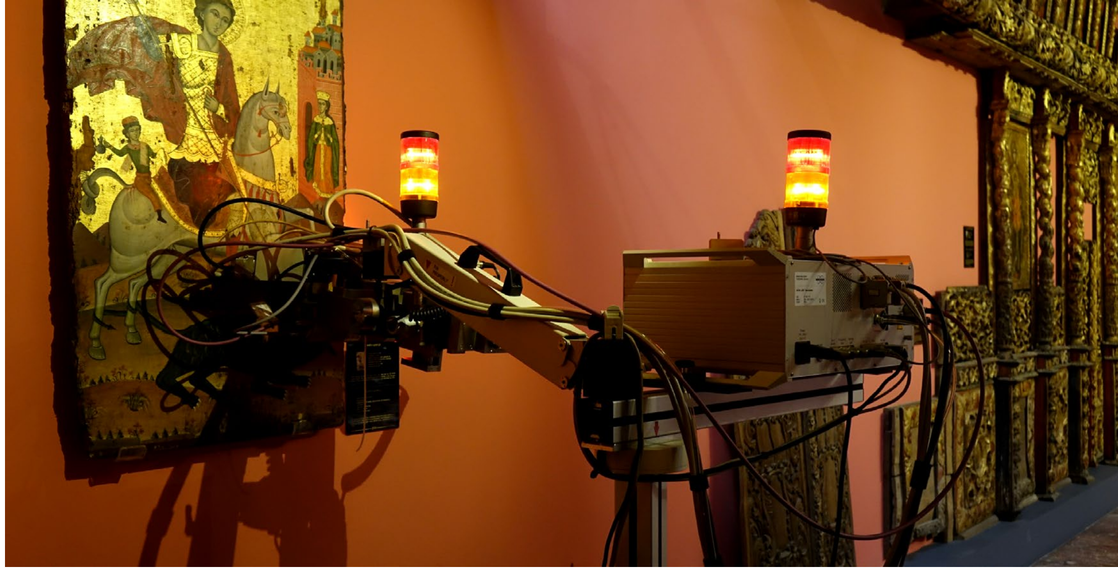
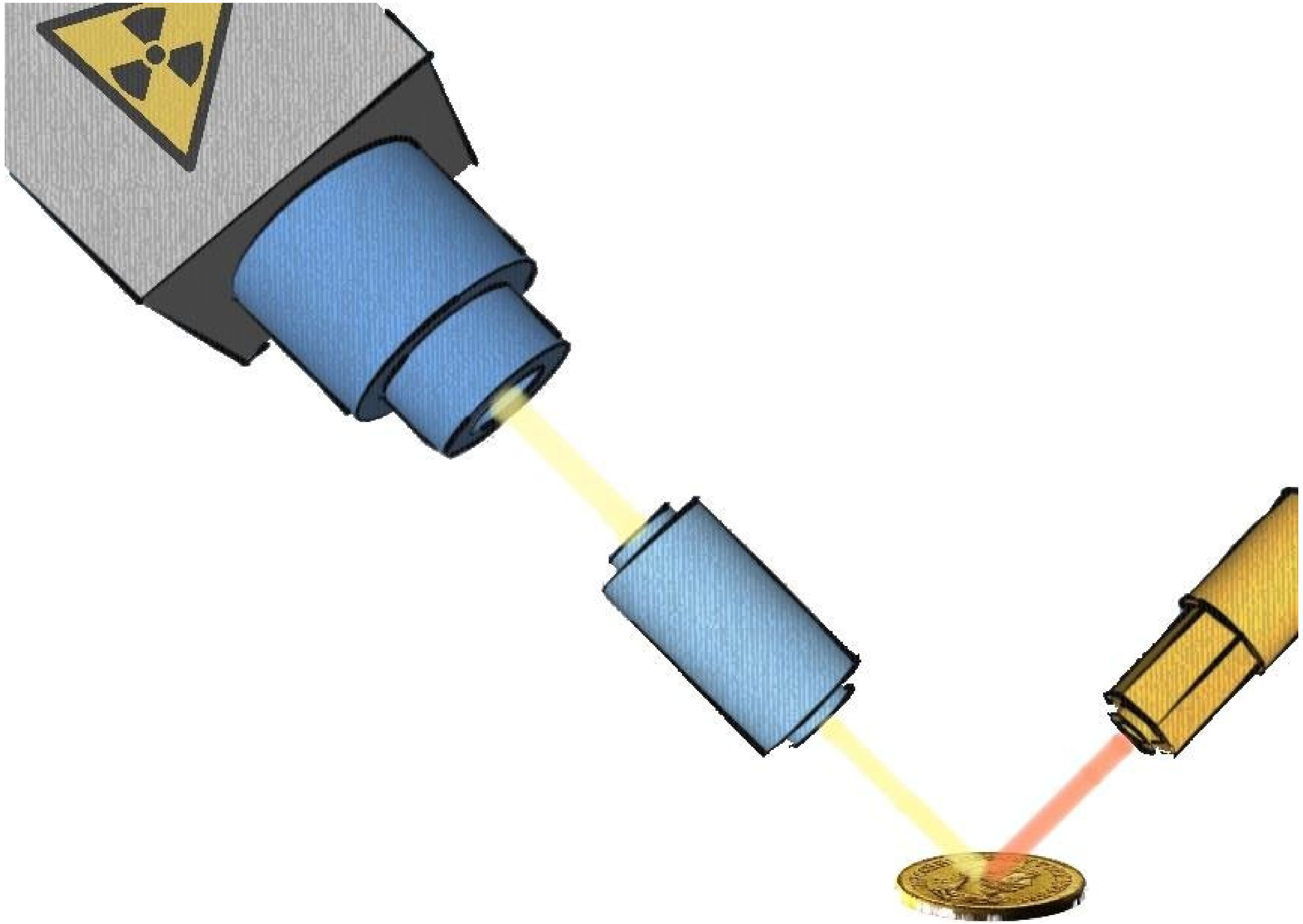
Introduction



Application of XRF spectrometry in Cultural Heritage

Non-Destructive
Sample preparation prior to study is not necessary
Works perfectly in room condition (air atmosphere)
Does not change the nature of the sample during the analysis
Short measurement time
Portable Instruments

low Z elements are very difficult to be detected (Z<13, Al)



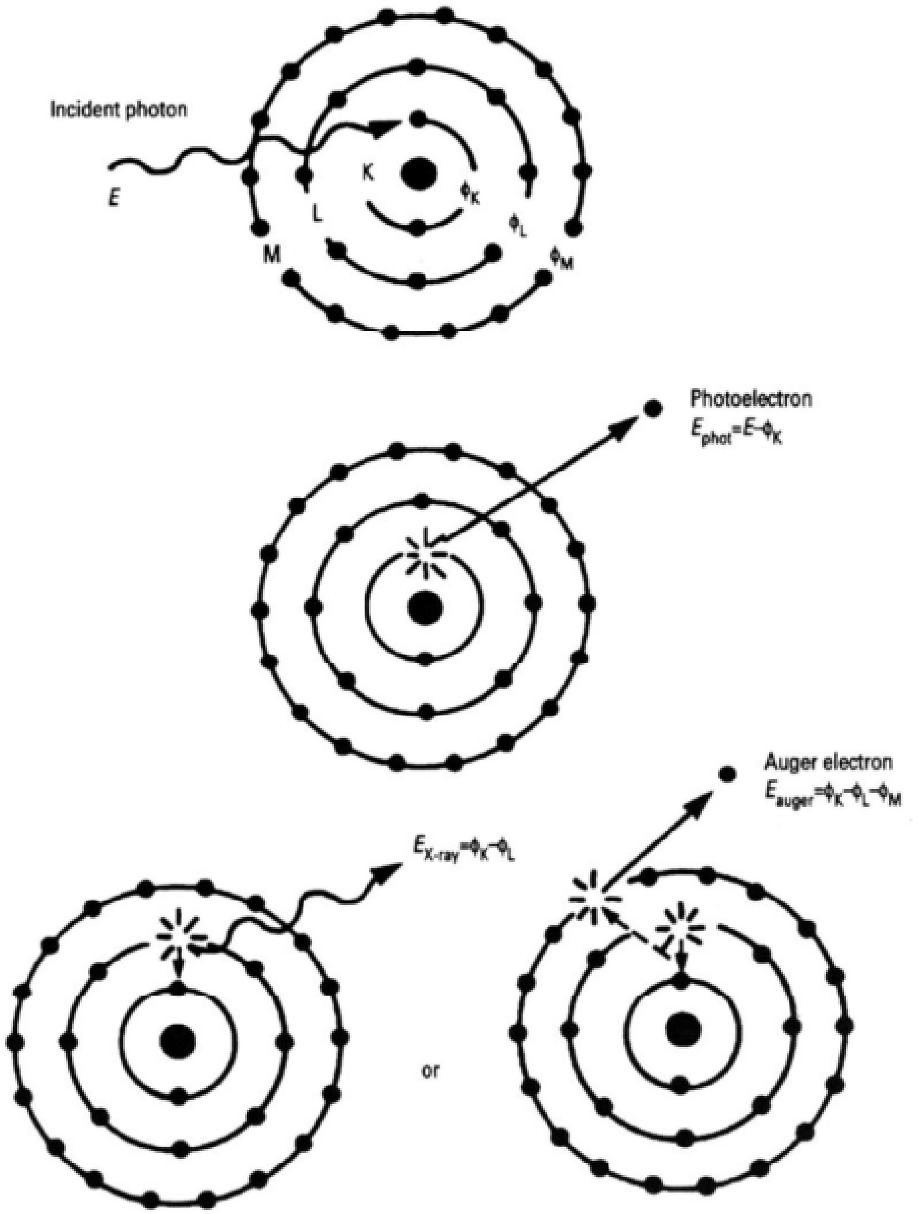
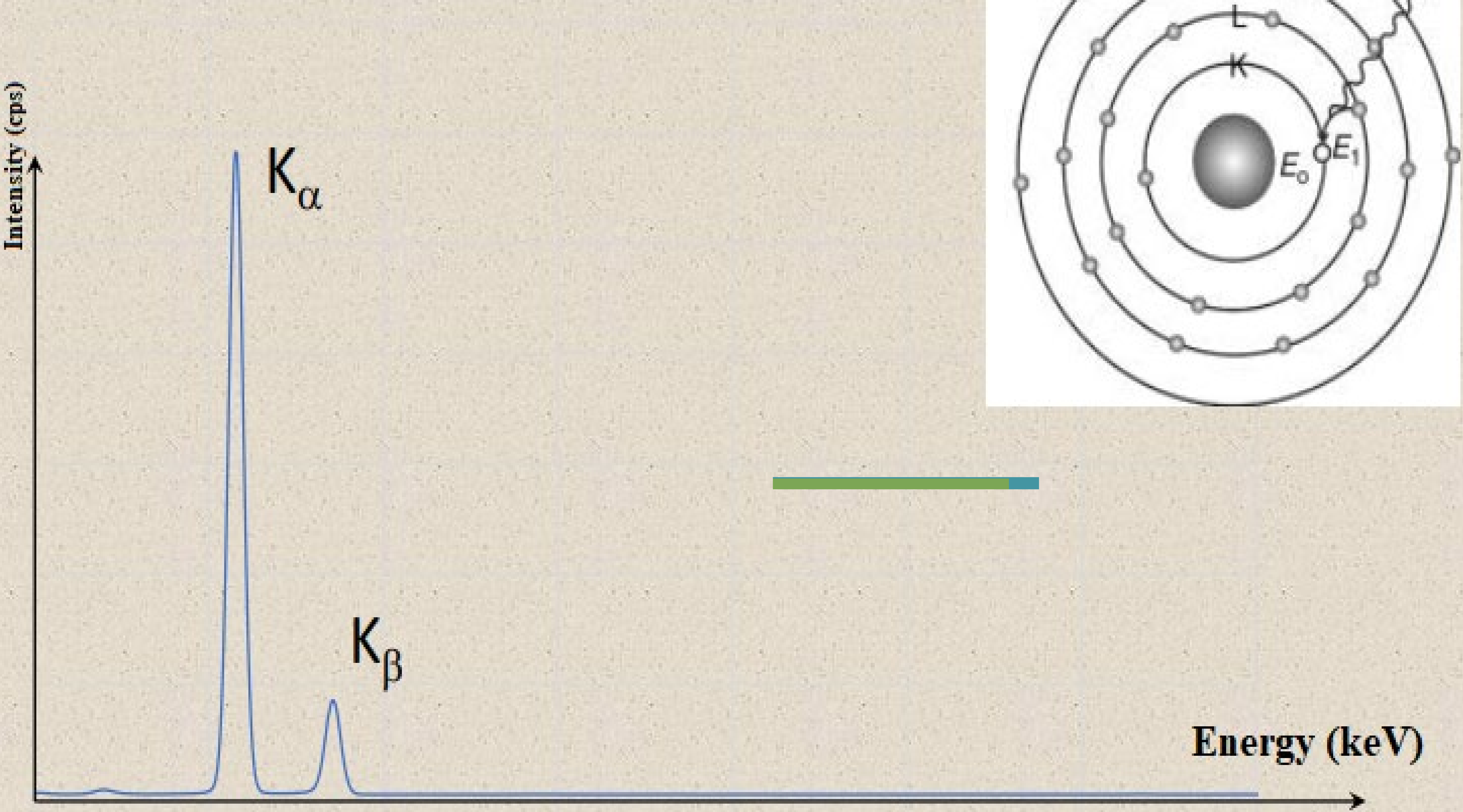


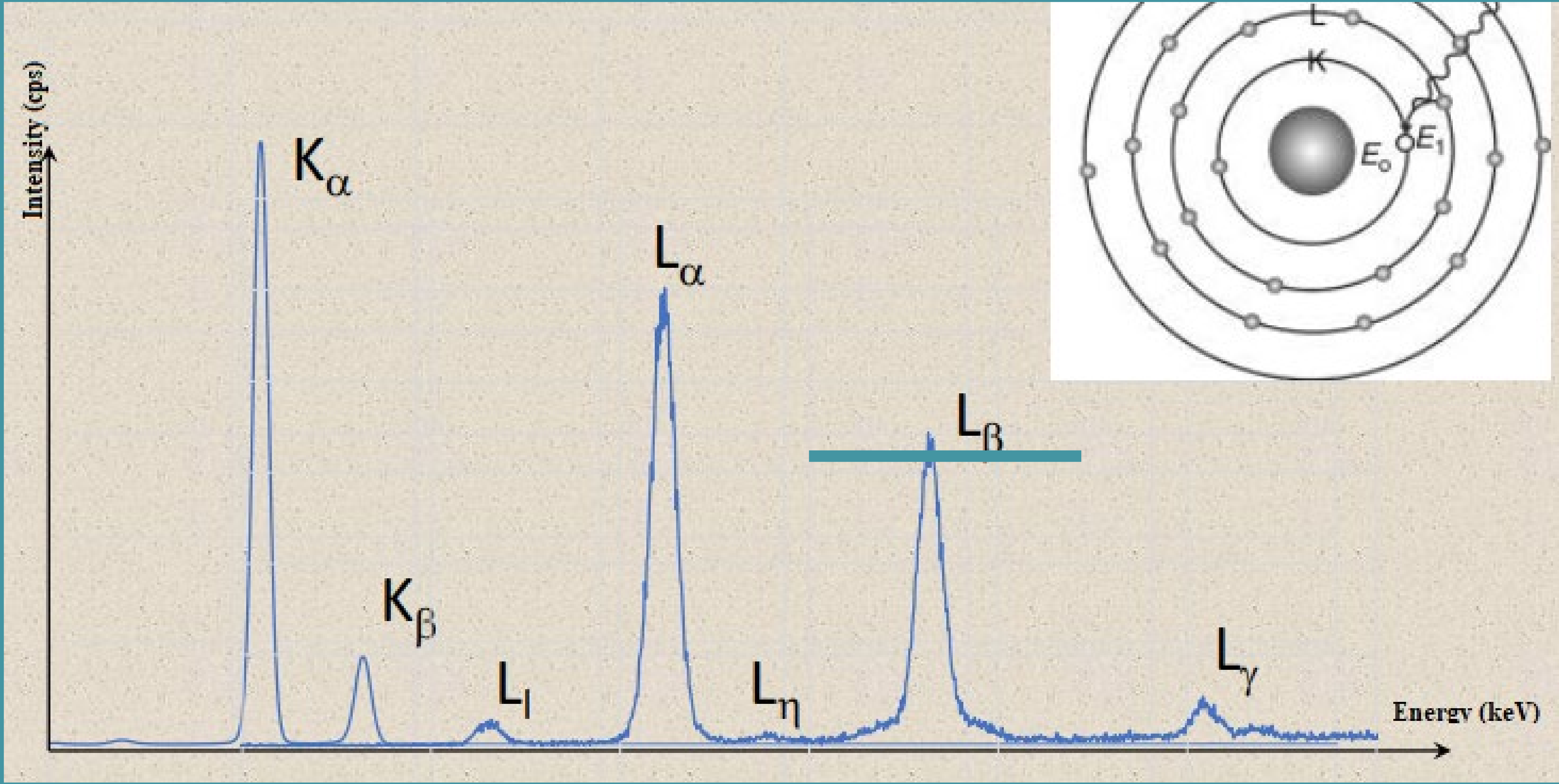
Fig. 11.3 Photoelectric ionization can be followed by either radiative relaxation, causing the emission of characteristic fluorescent X-rays or non-radiative relaxation, involving the emission of Auger electrons.

Characteristic X-ray emission and other effects

Characteristic X-ray fluorescence

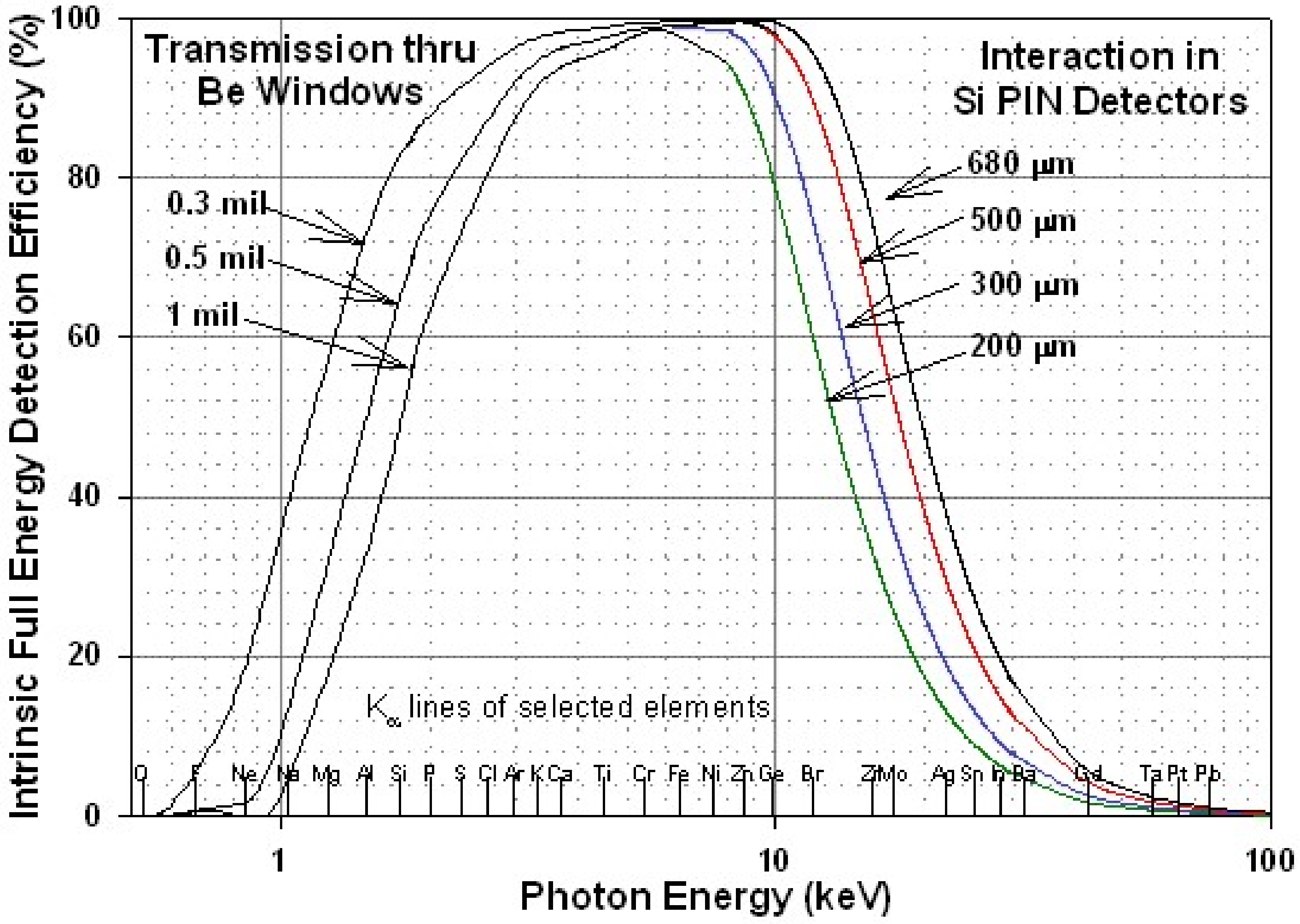
Auger electrons


L
K
E0
E1
Intensity (cps)
Kα
Kβ
Energy (keV)



Intensity (cps)
Energy (keV)
Kα
Kβ
Ll
Lα
Lη
Lβ
Lγ
L
K
Eo
E1

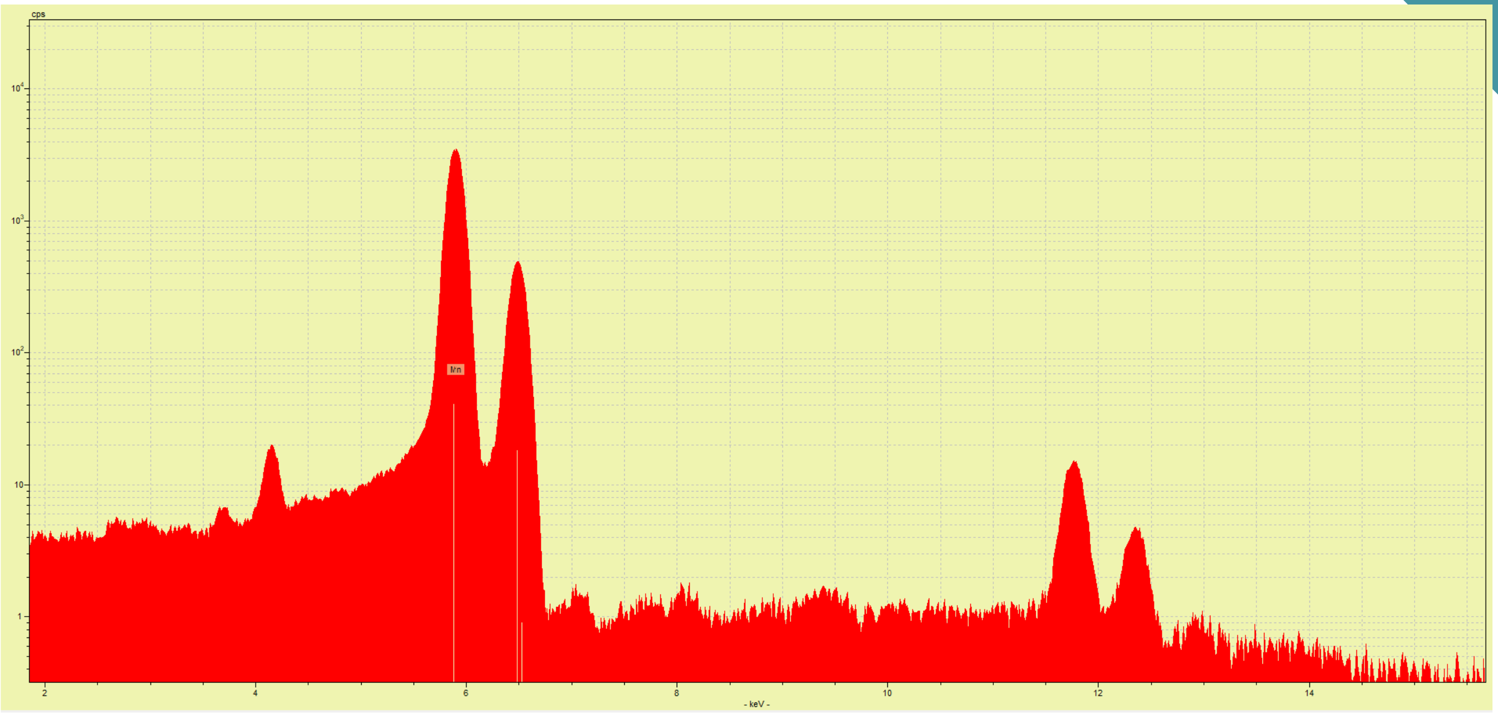
Energy Dispersive X-ray detection



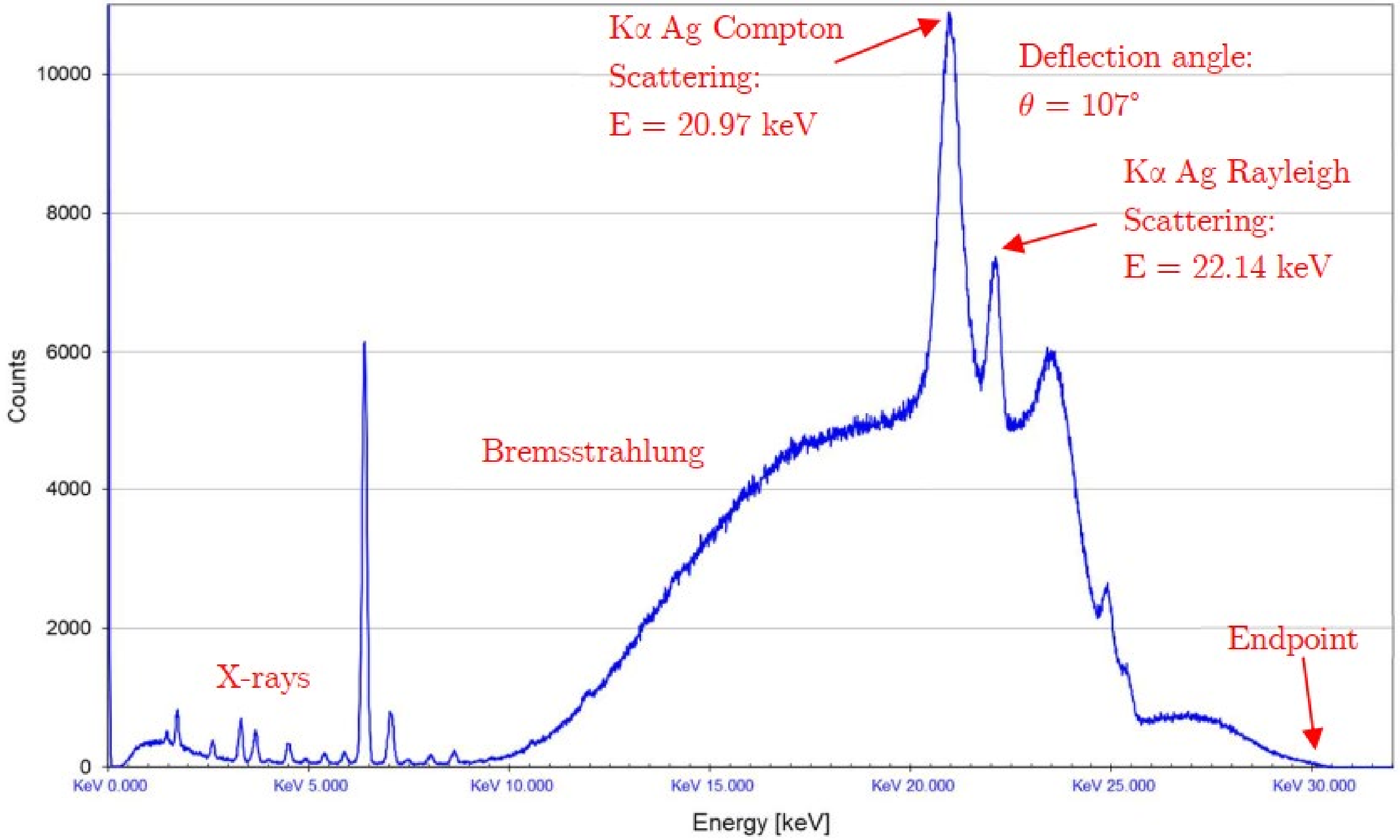
- The X-ray detection is carried out using a silicon drift detector (X-Flash 1000B), which provides a resolution of 146 eV FWHM at 10 kcps.
- This is coupled with a digital signal processor for accurate processing of the collected data.

Detector Resolution

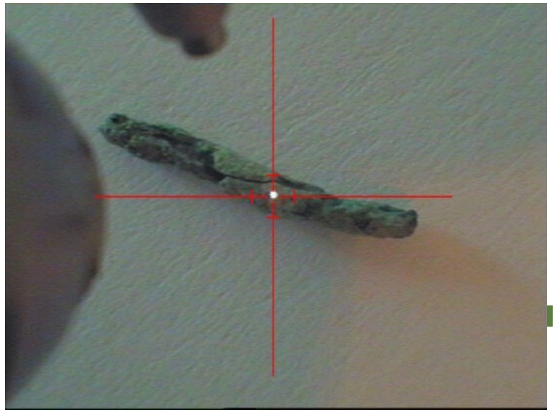
Date/Time:	01/10/2024 21:37:39
Channel count:	4096
Energy absolute:	-1.2383 keV
Energy linear:	0.012848 keV/ch
FWHM Mn-K:	147.31 eV
Fano factor:	0.11

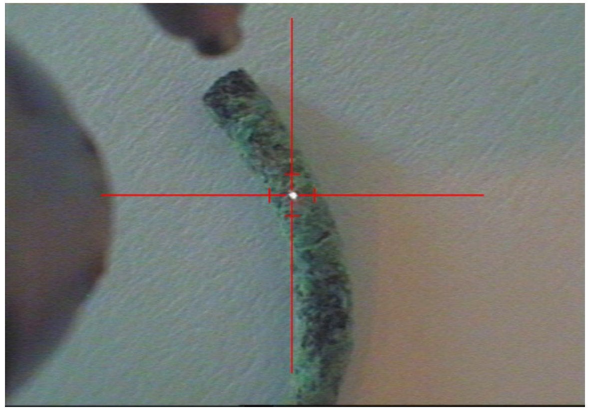


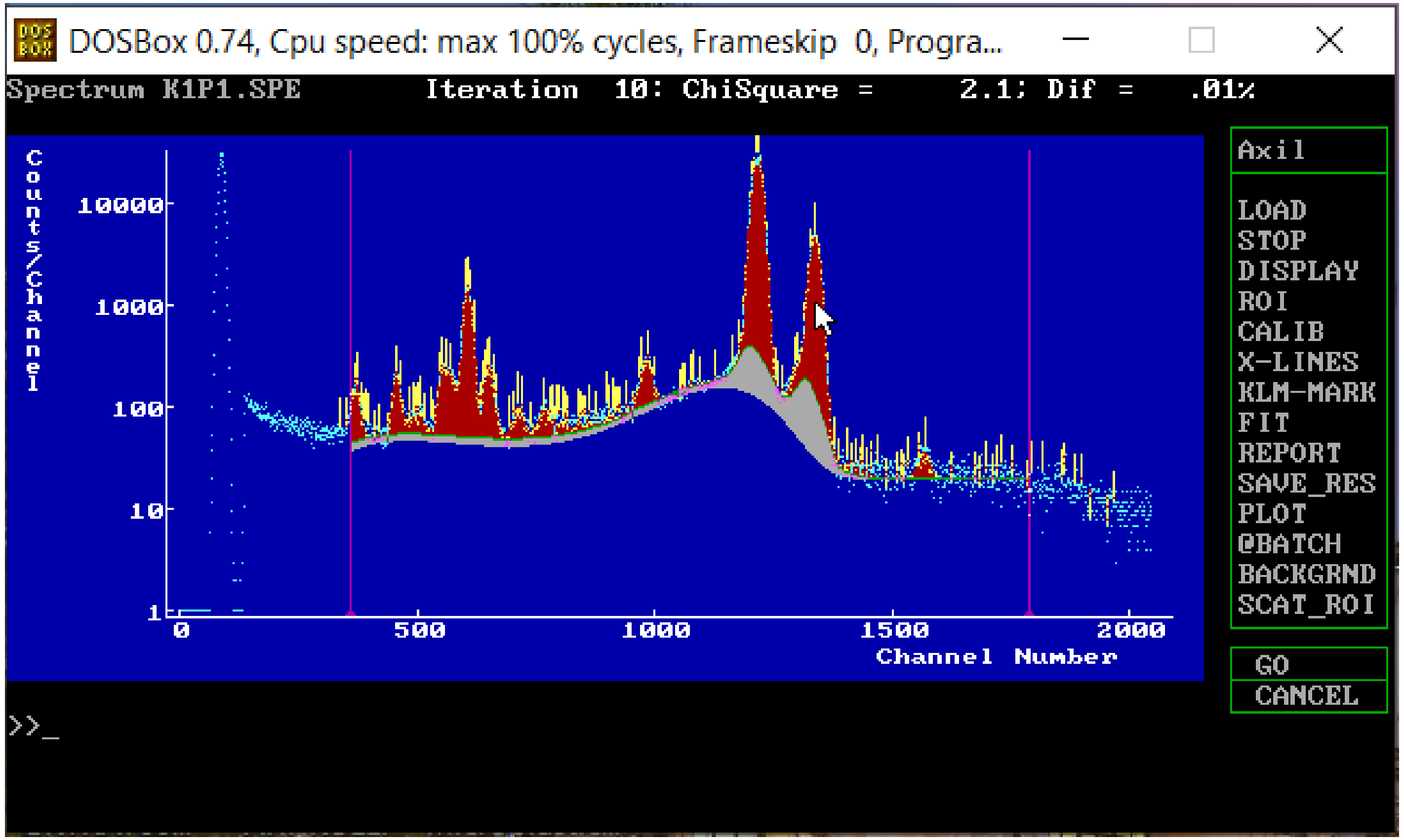
Characteristic spectra



Qualitative analysis







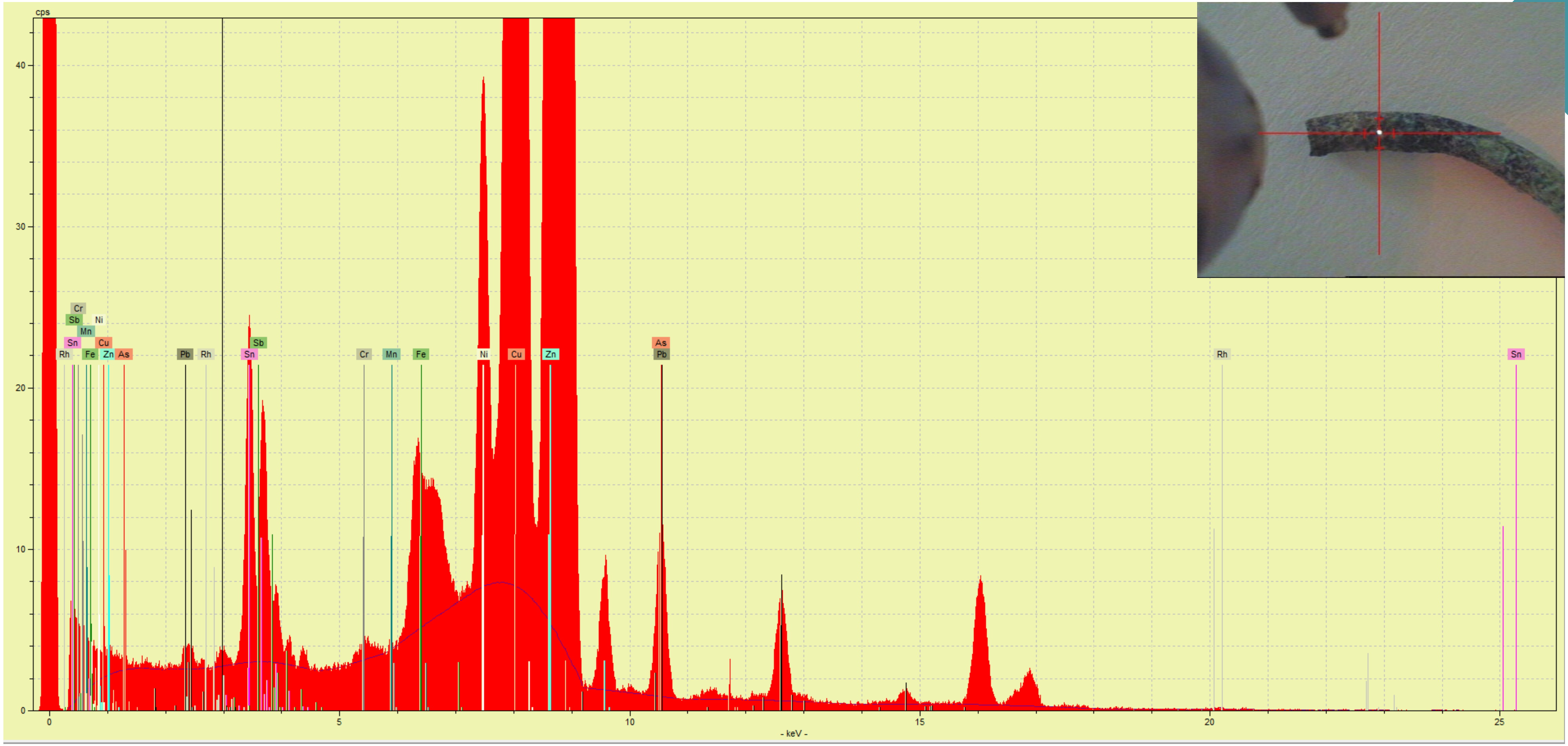
- We first conduct the qualitative analysis of the artefact samples using ARTAX and AXIL software.
- Qualitative analysis using XRF spectrometry gives insights on elemental compounds of materials used in: Pictures, frescoes, miniatures, pigments, artefacts.

Qualitative analysis

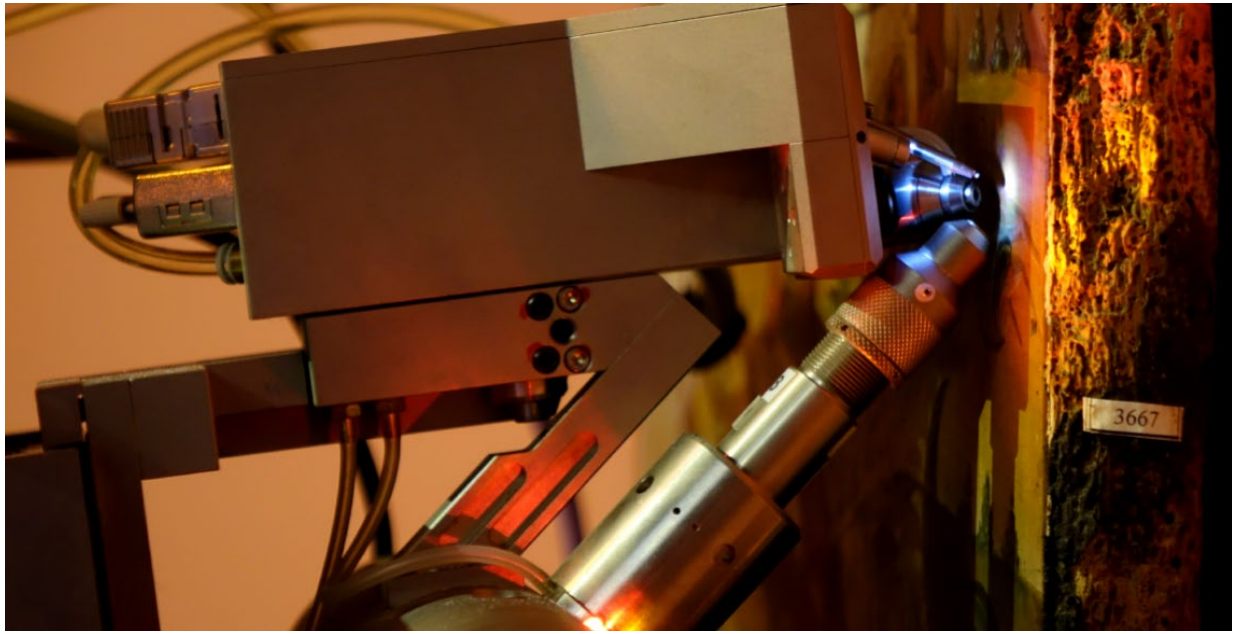
- The artifact is recovered from the Acropolis site in the city of Durrës. It represents an earring that was discovered by restoration specialists and archaeologists in an ancient grave.

- Social and economic situation of Dyrrhachium at those times is presented as follows; as part of the Byzantine Empire, the Illyrian-Arbërian lands faced the barbarian invasions. A relative calm was created that lasted until the first decade of the 6 century. This affected the preservation of the compactness of the urban and rural population (Qerimi, 2024). In order to date archaeological findings layer by layer, a great interest has arisen in fortifications and identification of the chronological periods of their construction, which started from the XIX century and has continued without interruption (Shehi, 2016).

Qualitative analysis



Quantitative Analysis



- The XRF instrument used for this study is the ARTAX μ-XRF spectrometer model 800 manufactured by Bruker.
- This device is equipped with a Rhodium (Rh) anode material and operates in direct excitation mode, ensuring precision in the detection process.
- During the measurements the generator was operated at 30 kV and 200μA, and the samples being measured for 50s with a dead time of 6%.

Quantitative Analysis

- The artefact was suspected to be devided on 9 pieces. The analysis was carried out at multiple points across the surface of the artifact.

- Specifically, we analyzed 3-4 points on each of the nine pieces that make up the earring. This thorough examination was essential to ensure that the results were consistent across the entire artifact and to verify whether the different pieces could be conclusively linked.
- For the quantitative analysis, we used the M-Quant software from Bruker, which relies on the fundamental parameter approach for accurate measurements. This method is recognized for its high reliability in determining precise concentrations of elements, particularly in historical artifacts where precision is critical. To ensure the accuracy of our measurements, we calibrated the XRF instrument using a brass standard from the IAEA proficiency test in 2013.
- Each measurement was further processed in the QXAS software provided by the IAEA, using the Full Fundamental Parameters (FFP) approach.

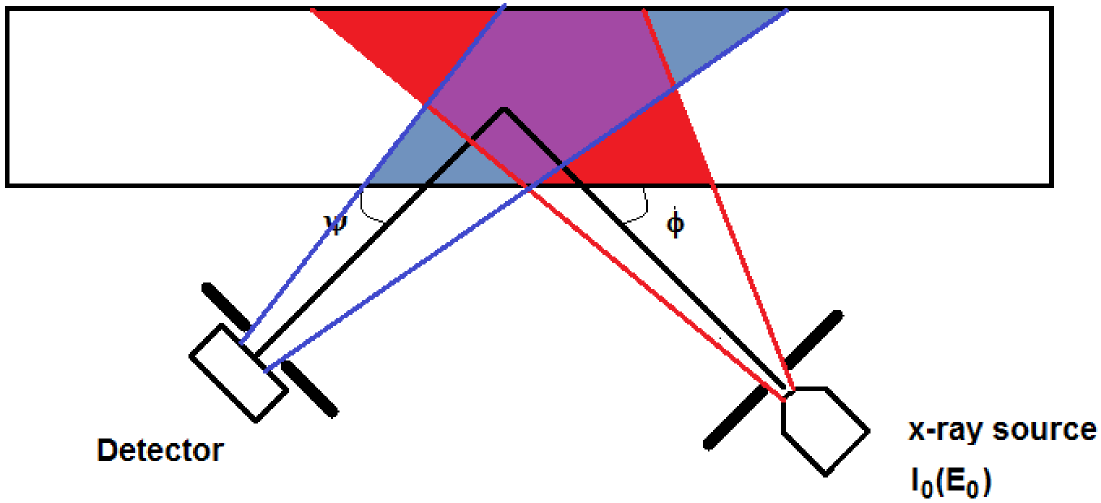
Full Fundamental Parameters Method

$$I_i \leftrightarrow C_i$$

Hypothesis

- Determined angles in the sample's surface
- Collimated beam
- Microscopic cross-section and homogenized surface
- Monochromatic Excitation
- Infinite thickness sample compared with X-rays pinging depth
- No peak overlay, no peak artefacts
- Incidence angle = Take off angle

Full Fundamental Parameters Method



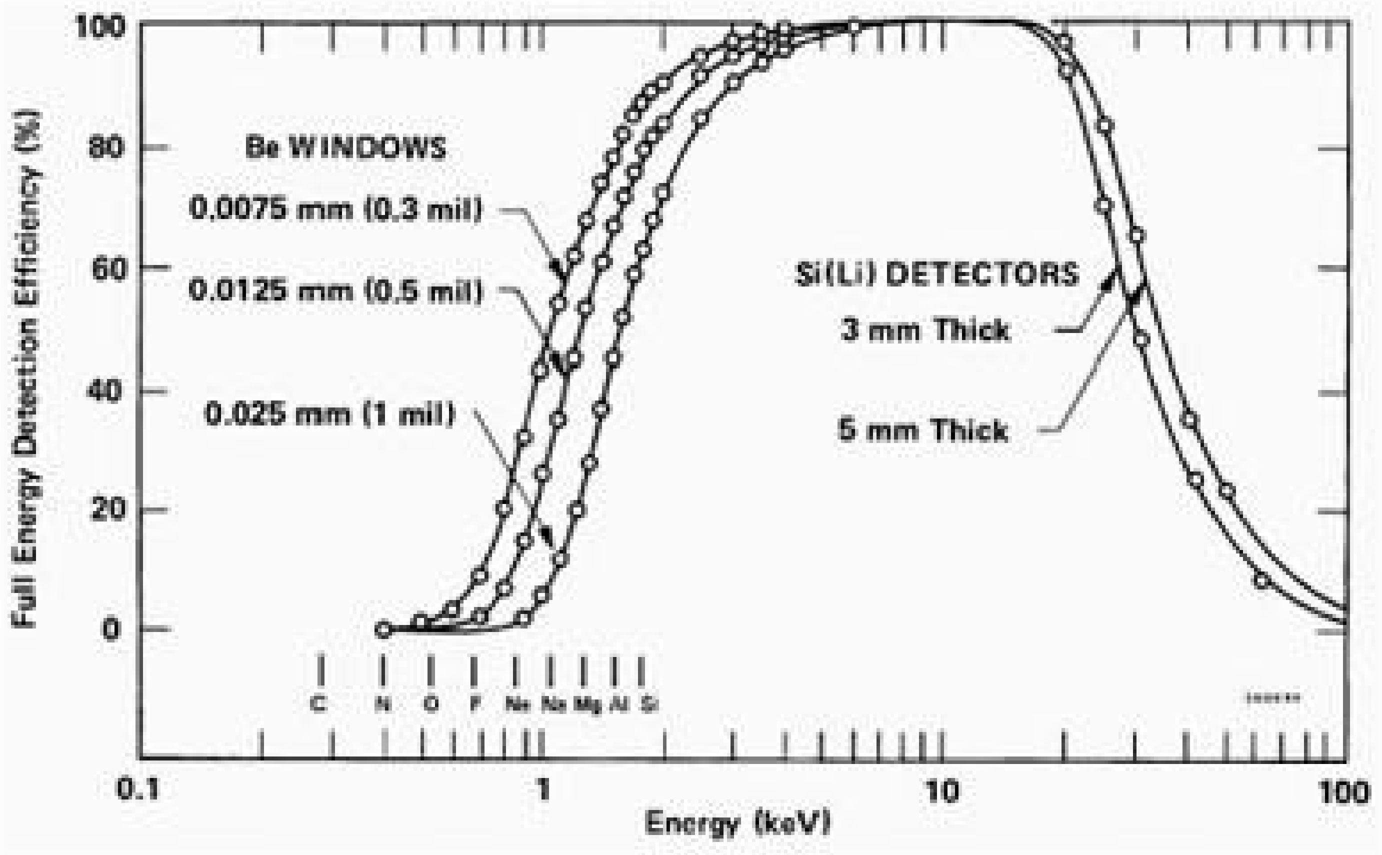
$$I_i \leftrightarrow C_i$$
$$I_i = C_i I_0$$
$$I_i = C_i I_0 P_i$$
$$P_i = \mu_{ph}(E_0)\left(1 - \Gamma_k^{-1}\right) w_{k,i} f_i$$

P_i is the probability for the production of X-rays that corresponds with the characteristic line of the ***i*** element being excited from the incident radiation

- $\mu_{ph}(E_0)$: Coeff of Photoelectric occurrence for the i-th element during the radiation with I_0
- $\left(1 - \Gamma_k^{-1}\right)$: % of photo-effect occurrence for the K shell
- $w_{k,i}$: Fluorescence yield of K shell for the i-th element
- f_i: Relative intensity for K lines on the energy E_i

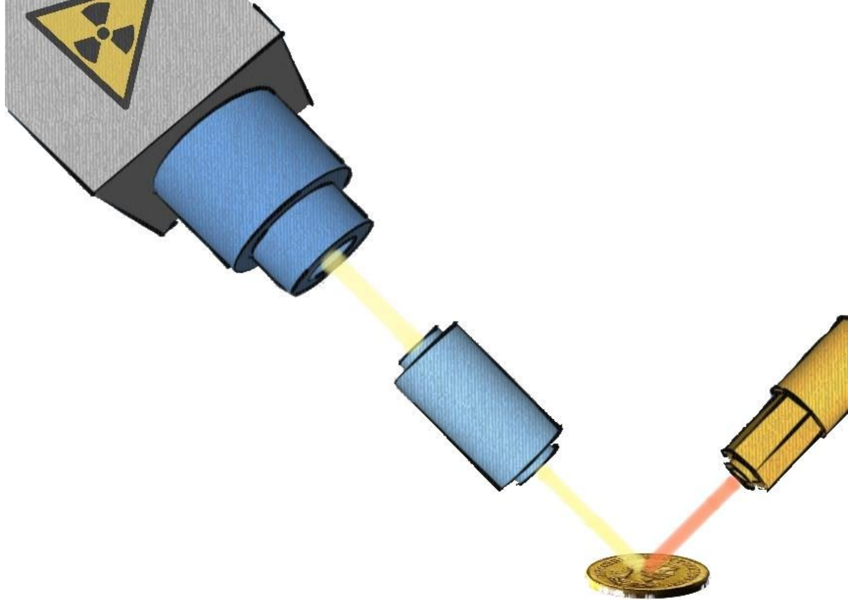
We are not done yet!

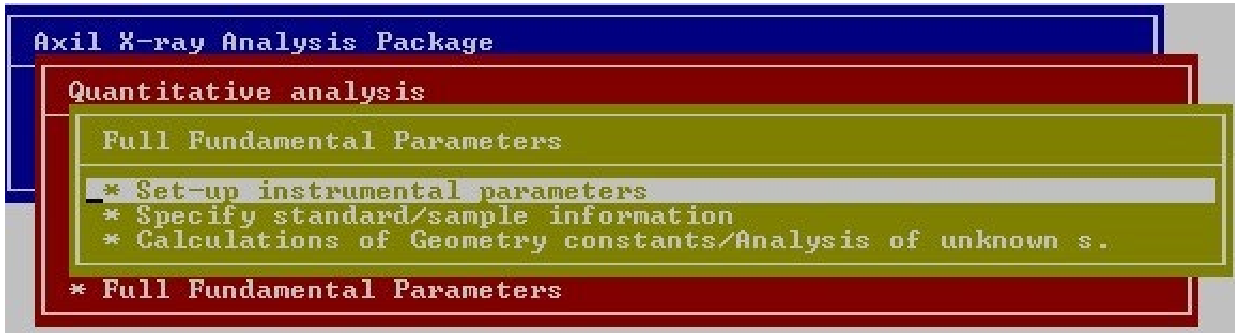
$$I_i = C_i I_0 P_i \varepsilon_i$$



The Geometry constant of the system

$$I_i = C_i I_0 P_i \varepsilon_i G$$





Corrections for the Matrix Effects

Attenuation coefficients

Enhancement coefficients

$$I_i = C_i I_0 P_i \varepsilon_i G \left[\frac{1}{\sum_{j=1}^{n} c_j \mu^*_{j,E_0} + \sum_{j=1}^{n} c_j \mu^*_{j,E_i}} \right]$$

Attenuation coefficient of the excitation caused from Anode (Incident radiation)

Attenuation coefficient of the excitation caused by the i-th element. (consider this for all elements toward each other)

Who is getting bored?

I_i intensity of characteristic X radiation emitted from the atom of the element "i“.

I_0 incident radiation intensity

P_i product of atomic factors

ε_i detector efficiency coefficient at energy E_i

G geometric efficiency coefficient

C_i concentration of the i - element

μ_i photoelectric absorption coefficient of element “i” for X-ray radiation of energy E_0

E_0 monochromatic excitation energy

E_i characteristic emission energy

FFPM for metal alloys

To determine all these coefficients related to experimental conditions, we first measure a standard material with known concentrations and with a similar matrix as the sample.

$$I_i = C_i I_0 P_i \varepsilon_i G \left[\frac{1}{\sum_{j=1}^{n} c_j \mu_{j,E_0}^{*} + \sum_{j=1}^{n} c_j \mu_{j,E_i}^{*}} \right]$$

↕

$$\frac{I_i}{I_0} = R_i = C_i \left[\frac{\mu_{i,E_0}^{*} + \mu_{i,E_i}^{*}}{\sum_{j=1}^{n} c_j \mu_{j,E_0}^{*} + \sum_{j=1}^{n} c_j \mu_{j,E_i}^{*}} \right]$$

Results

This is a representation of AXIL quantitative analysis report designed for DOS systems.

FUND4 09-30-2024 22:55:03

Sample identity: NO_ID
Spectrum fitting data: C:\SPECT\VATHI\KPASR\K2P2.ASR
Instrument parameter data: C:\SPECT\BRONZ.FPC

Instrumental identity: X-Ray Tube
Average instrumental constant: 3.4028E-06
Tube anode: Rh
Tube voltage: 30. KV Tube current: .200 mA
Measuring time: 200. Sec. Collimator: No Collimator
Filter used: No Filter Atmosphere: Air

Report of Calculated Concentrations

Sample thickness: infinitely thick
Iterations for concentration: 5
Pre-set convergence: .10 % Last convergence: .070 %

Ele.-line	Constituent		Concen.(elem.)		Absorption	Enhancement
P -Ka	P	22.26ñ	2.869	%	4.0173E-04	1.6523
Cl-Ka	Cl	2.07ñ	.347	%	6.1851E-04	1.6443
Ar-Ka	Ar	1.99ñ	.158	%	8.0711E-04	1.6539
K -Ka	K	7605.78ñ	733.339	ppm	9.4309E-04	1.6530
Ca-Ka	Ca	4.96ñ	.083	%	1.1751E-03	1.6524
V -Ka	V	1422.61ñ	124.081	ppm	2.0207E-03	1.7036
Cr-Ka	Cr	4447.63ñ	109.338	ppm	2.3695E-03	1.7306
Mn-Ka	Mn	250.06ñ	56.891	ppm	2.7221E-03	1.7783
Fe-Ka	Fe	2671.22ñ	70.515	ppm	3.1092E-03	1.8312
Cu-Ka	Cu	61.16ñ	.077	%	4.0563E-03	1.0011
Zn-Ka	Zn	2630.84ñ	87.289	ppm	3.8646E-03	1.0011
Rh-La	Rh	3.44ñ	.741	%	6.3700E-04	1.0448
Sn-La	Sn	8042.99ñ	2193.543	ppm	9.1656E-04	1.0458
Ba-La	Ba	6199.56ñ	695.660	ppm	1.4507E-03	1.0464
La-La	La	3179.21ñ	407.591	ppm	1.5883E-03	1.0478
Er-La	Er	3000.48ñ	296.056	ppm	3.3660E-03	1.0063
W -La	W	289.52ñ	59.548	ppm	5.1065E-03	1.0009
Pb-La	Pb	1520.06ñ	95.004	ppm	3.8870E-03	1.0004

Results

From the analysis, the pieces of the artefacts resulted to have this compounds:

Elements	**Concentration with Stand. dev**
P	9.5 % $\pm$ 2.554 %
Ca	7.18 % $\pm$ 0.095 %
Fe	5.12 % $\pm$ 0.021 %
Ni	587.88 ppm $\pm$ 79.979 ppm
Cu	64.1 % $\pm$ 0.067 %
Zn	4032 ppm $\pm$ 99.202 ppm
Sn	12.33 % $\pm$ 0.303 %
Pb	839 ppm $\pm$ 93.529 ppm

Discussions

- The all elements mentioned are part of the composition of the Bronze metal alloys despite of Ca comes from the deposits of layers of soil on the artifact over the years.

- Our results indicate that all the pieces of the earring are indeed part of the same object. This conclusion is based on the fact that the elemental analysis revealed nearly identical chemical compositions across all the pieces. In particular, the ratios of copper (Cu) and tin (Sn), the two primary components of bronze, were consistent across the different parts of the earring. This uniformity in composition strongly supports the hypothesis that the separate pieces were originally part of a single, unified object.

- The only exception is sample nr.4 which seems to be from a different origins as the ratios of Cu/Sn are inversed.

- In conclusion, the use of X-ray fluorescence for both qualitative and quantitative analysis has allowed us to make significant progress in understanding the artifact's origins and structure. This research not only confirms that the earring fragments belong to the same object but also provides valuable insights for future studies on ancient artifacts in Albania.

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Thank you!

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