

Advanced Physics Laboratory:
X-Ray Fluorescence (XRF)

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1. Introduction

X-ray fluorescence (XRF) spectrometry is an elemental analysis technique with broad application in science and industry. It's one of the most common non-destructive methods for qualitative as well as quantitative determination of elemental composition of materials. XRF is based on the interaction between X-ray and matter which in turn emit a so-called characteristic radiation (fluorescence) that is unique for every element. By counting the number of photons of each energy emitted from a sample, the elements present can be identified and quantitated. The methodological technique used in our experiment is commonly known as energy dispersive X-ray fluorescence (EDXRF), where the energy spectrum is collected and recorded simultaneously by a silicon drift detector (SDD). The range of detectable materials covers all elements that can be excited by the X-ray source energy. Detection limit depends upon the specific element and the sample matrix but in general heavier elements have higher detection limit.

2. Fundamentals

2.1. X-ray production

X-rays make up X-radiation, a form of high-energy electromagnetic radiation. Most X-rays have a wavelength ranging from around 150 Å down to less than 0.02 Å, corresponding to energies in the range between around 100 eV to few hundreds of kilo electron volts, keV, (lying between ultra-violet and gamma radiations). The wavelength, λ , of a given photon and its energy E are correlated by:

$$E = \frac{hc}{\lambda}$$

Where h is the Planck's constant and c is the speed of light.

X-rays can be produced by a radioactive source, an X-ray tube or a synchrotron radiation. In the present experiment, we use an X-ray tube. A typical X-ray generator is mainly formed of a

filament as a cathode, connected to a high voltage generator and an anode material. The emitted electrons from the cathode due to the electrical current through the filament (glow emission) are accelerated by a high electric field towards an anode, emitting photons in the X-ray range (fig. 1 (a)). The X-ray emission spectrum obtained from an X-ray tube with a tungsten anode is shown in Figure 2 (b) for different applied voltages.

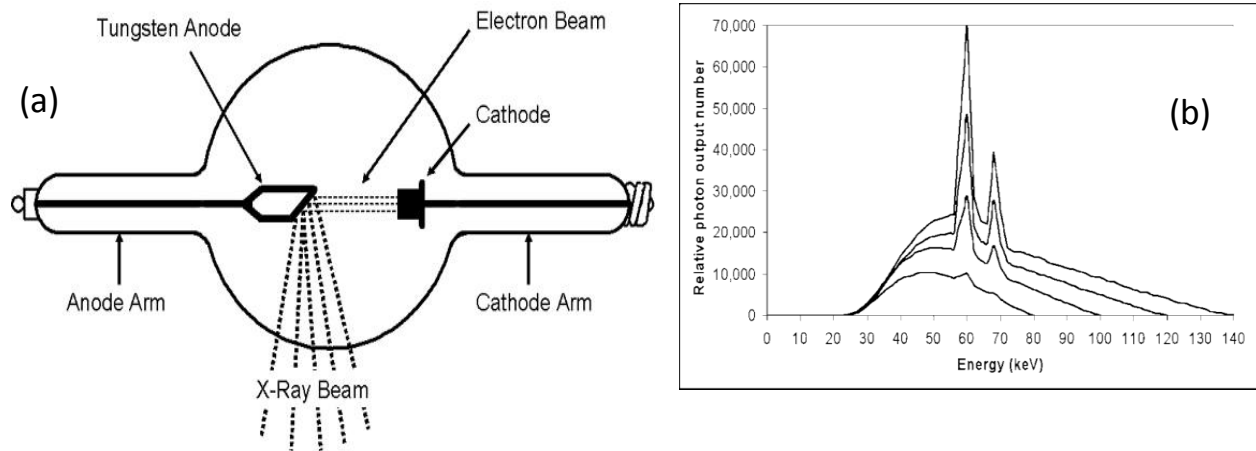


Figure 1: (a) scheme of X-ray tube with tungsten target material (anode). (b) X-ray emission spectra produced by this tube at different voltages.

As can be seen in figure 1 (b), the X-ray spectrum of the tube contains in addition to the *continuous radiation*, two peaks referring to the emission lines of the target material of the tube, here tungsten. Such lines are called *characteristic radiation*.

- **Continuous radiation:** The continuous radiation (also known as *Bremsstrahlung*) is the result of the deceleration of the electrons by the anode material of the X-ray tube, and it has a maximum energy equal to the maximum applied high voltage, related by:

$$E_{max} = eU$$

Where E_{max} is the maximum energy in the output spectrum, e is the electron charge and U is the applied voltage. As example, if the applied high voltage by the generator is set to 40 kV, the maximum X-ray energy obtained in the spectrum will be 40 keV.

- **Characteristic radiation**

If an electron of an inner shell is separated from the atom by the irradiation of energy, an electron from a higher shell falls into this resultant “hole” which releases an amount of energy equivalent to the difference between the energy levels involved. The energy being released can be either emitted in the form of an X-ray (fig.2), or transferred to another atomic shell electron (Auger effect). The probability of an X-ray resulting from this process is called the fluorescence yield ω . This depends on the element’s atomic number and the shell in which the “hole” occurred. ω is very low for light elements (approx. 10^{-4} for boron) and almost reaches a value of 1 for the K-shell of heavier elements (e.g. uranium). However, since the energy or wavelength of the X-ray is very characteristic for the element from which it is emitted; such radiation is called characteristic X-rays. This provides the basis for determining chemical elements with the aid of X-ray fluorescence analysis

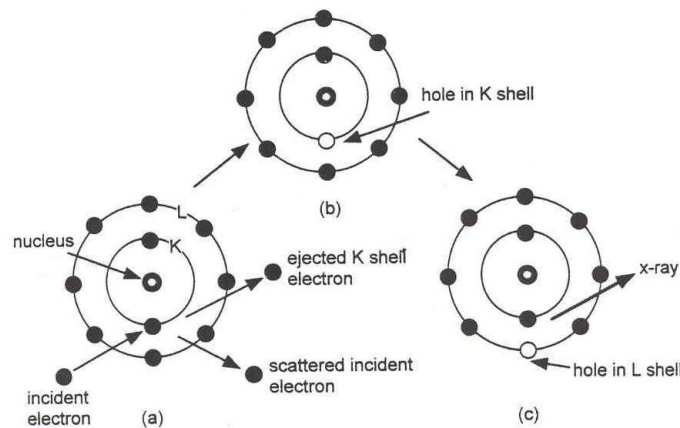


Figure 2: Production of characteristic lines from an X-ray tube.

2.2 Interaction of X-rays with matter

Once the atom exposed to radiation with energy $E < 1022$ keV, two types of interactions can occur: the photoelectric absorption and the Compton Scattering. When $E \geq 1022$ keV, a pair production process can take place.

- **Photoelectric effect:** When the incident photon energy E is larger than the binding energies B_e of atomic electrons, photons can be completely absorbed by the atom, accompanied with ejection of an electron raised into a state of the continuous spectrum. This process is called photoelectric effect. The ejected electron is emitted with a kinetic energy equal to the difference between the incident photon energy and the binding energy of the electron:

$$K_e = E - B_e$$

When absorption occurs, only a certain fraction of the incident radiation (I/I_0) may pass through the sample. In this case, the wavelength of the transmitted beam is unchanged and the intensity of the transmitted beam is given by the *Lambert-Beerschem* equation:

$$I = I_0 e^{-\mu x}$$

Where x is the thickness of the sample (absorber) and μ_a is the attenuation coefficient of the absorber at the incident wavelength/energy.

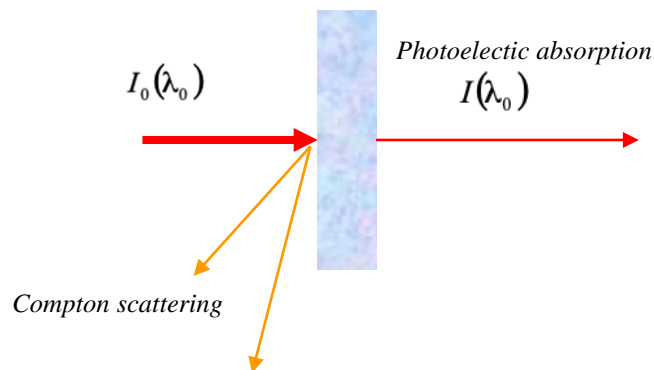


Figure 3: Interaction of X-ray photons with matter

- **Compton effect:** When the incident photon energy E is much larger than the binding energy of the K-shell electron B_e such that the ratio B_e / E can be neglected, Compton scattering

becomes the dominant process. The Compton effect is an incoherent scattering process based on the corpuscular behaviour of the incident photons on individual atomic electrons. Furthermore, it is considered as an inelastic process, although the kinematic description of the reaction is that of an elastic collision. When the incoming photon with energy E is scattered by a quasi-free electron, it emerges at an angle θ with energy E' :

$$E' = \frac{E}{1 + \epsilon(1 - \cos \theta)}$$

2.3 Principle of the X-ray fluorescence process

Once the specimen is excited with the primary X-radiation, electrons from the inner electron shells are knocked. Electrons from outer electron shells fill the resultant voids emitting a fluorescence radiation that is characteristic in its energy distribution for a particular material (fig. 2). As mentioned above, Each element has its unique characteristic energy spectrum produced by all the allowed transitions of the specific atom following the X-ray excitation. XRF technique consists on the study of the produced characteristic spectrum. A scheme of XRF process inside the atom is shown in Figure 4(a), while in (b) some emission lines of As and Pb are also shown.

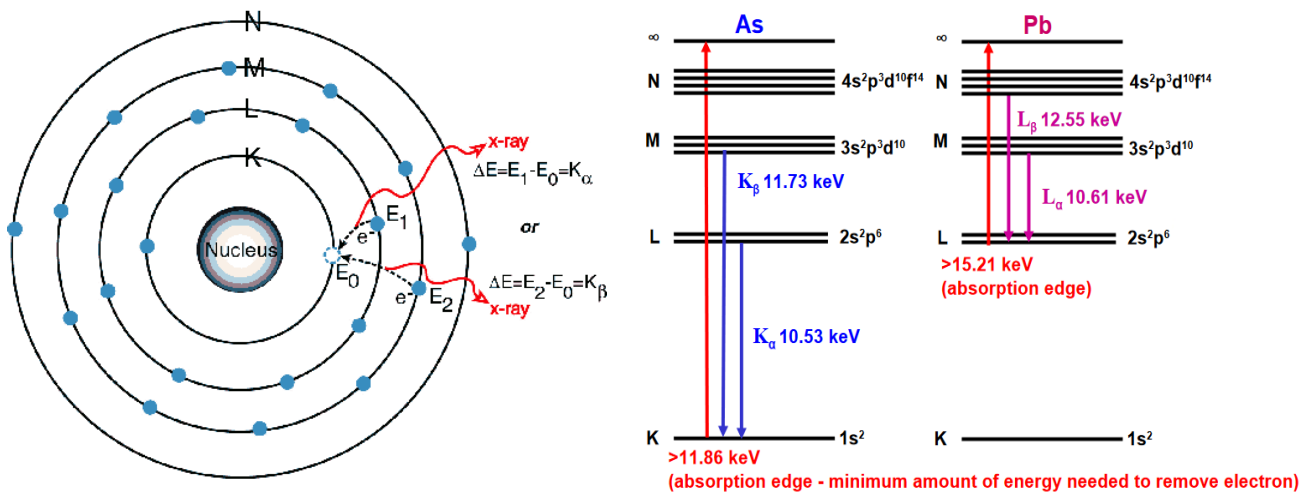


Figure 4: (a) fluorescence process and (b) emission lines of As and Pb

The energy of each transition from an atomic level m to an atomic level n is proportional to the square of their atomic number. The relation between the emission energy and the atomic number is described by an empirical law for the characteristic X-rays: Moseley's law:

$$E_{mn} = R_H (Z - \sigma)^2 \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

Where R_H is the Rydberg constant, Z is the atomic number and σ is the screening constant of the atom. Every element has its own characteristic radiation considered as its fingerprint. The energies of emission lines for all elements of periodic table are tabulated and can be found in Appendix A. Also they're available on many web pages such as:

http://fisica.uc.pt/data/20082009/apontamentos/apnt_339_10.pdf and

https://www.bruker.com/fileadmin/user_upload/8-PDF-Docs/X-rayDiffraction_ElementalAnalysis/HH-XRF/Misc/Periodic_Table_and_X-ray_Energies.pdf

As an example, figure 5 shows an energy spectrum of a sample containing copper and zinc, recorded by an energy dispersive detector. The main 4 peaks refer to the K-emission lines of both elements. The values on the horizontal axis represent the energy value of the emitted X-ray in ADU unit (channel number) that need to be calibrated later in the analysis and converted to a real energy unit, eV.

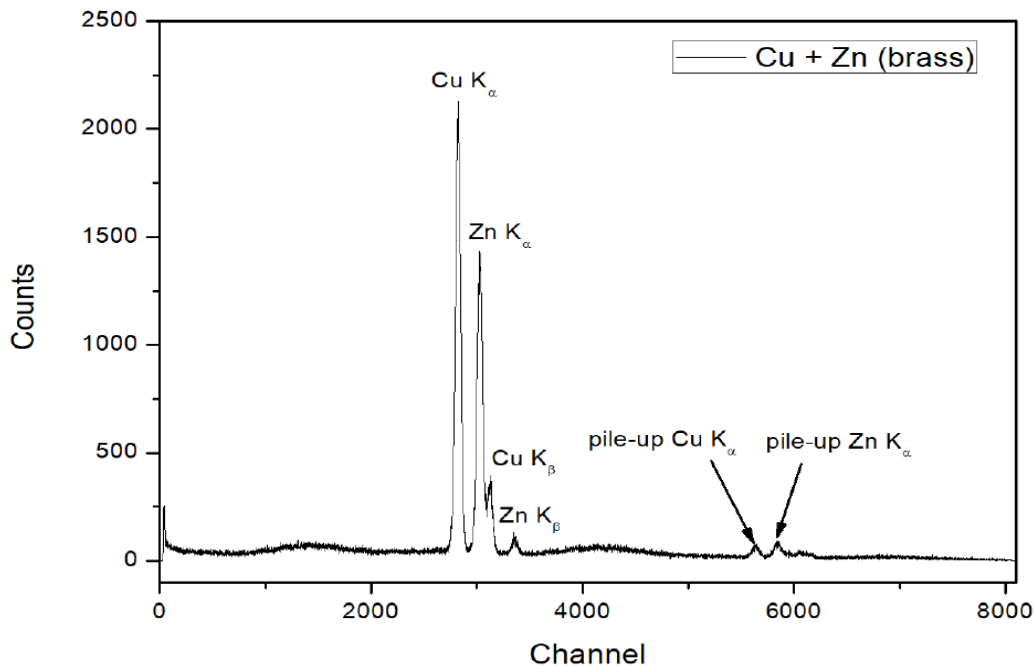


Figure 5: X-ray energy spectrum of a sample contains Cu and Zn.

3. Experiment and data analysis

3.1 Experiment setup

Figure 6 shows a scheme of a typical X-ray fluorescence spectroscopy arrangement which includes a source of a primary radiation (X-ray tube in our case), the investigated sample, SDD detector and a computer for acquisition and processing the recorded events.

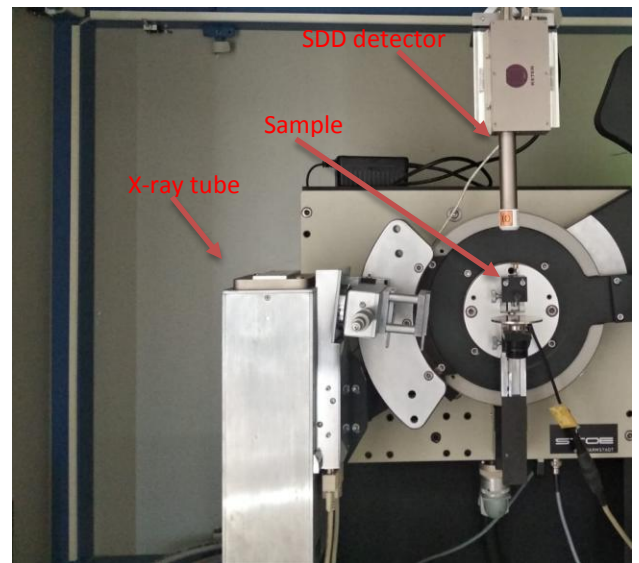
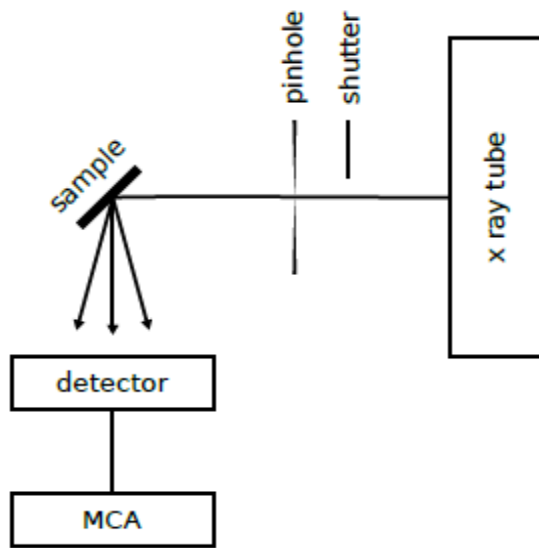


Figure 6: (a) A scheme of XRF experiment setup and (b) the real setup in the lab.

The X-ray tube used in our experiment has a copper anode. It can be adjusted to a maximum current of 50 mA and maximum energy of 60 keV. In order to prevent melting of the anode material, the anode is water cooled. A thin beryllium (highly transparent to X-rays) window is used to allow the X-rays out of the generator, and onto the sample.

The Silicon drift detector (SDD) works on the principle of the photoelectric effect in which any detected photons create a number of electrons equivalent to the photon energy. It consists of a fully depleted volume of silicon. An electric field is applied to drift the generated electrons towards a small sized collecting anode. As the device is fully depleted the entire thickness (0.45 mm in the SDD used here) is sensitive to the absorption of X-rays. Cooling of the device is ensured by a thermo electric cooler (Peltier effect). A scheme of SDD detector is shown in figure 7.

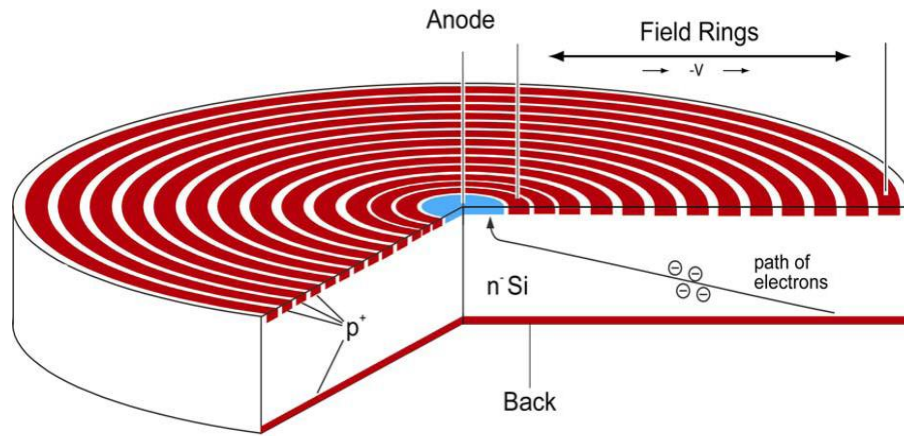


Figure 7: Scheme of the Silicon Drift Detector (SDD)

3.2 Objectives and tasks

The final aim of this experiment is to perform XRF measurement on some specimens, and then analyze the obtained spectra to find the elements involved in these samples and the concentration of every content.

The main tasks are:

3.2.1. Energy calibration of the SDD detector

The obtained fluorescence spectra need to be calibrated in energy. For that, reference samples have to be used such as a pure copper or a pure zinc. The well-known emission lines of these measured samples are then used to find a linear relation between the energy in eV and channel number of the detector (ADU). This calibration can be done directly during the measurement. However, the data is recorded only in ADU unit, and thus, a new calibration need to be done later during the data analysis.

As example, if the spectrum shown in figure 5 already known that it's belong to a sample formed of Cu and Zn, one can use these peaks and compare their positions at ADU (after Gaussian fit) with their values in eV from literature to perform the calibration.

3.2.2. Identification of characteristic lines from the X-ray tube

Since the anode material of the X-ray tube is formed of Copper, $Cu - K_{\alpha}$ and $Cu - K_{\beta}$ fluorescence lines are expected to be seen in the background spectrum. These background peaks are unavoidable once the applied voltage exceeds 8.9 kV (the minimum voltage required to emit

$Cu - K_{\beta}$ at 8.9 keV). However, the background spectrum should be subtracted later from the measured spectra of the samples to get accurate results.

3.2.3. Qualitative identification of the chemical composition of some alloyed materials.

After energy calibration of the detector and subtracting the background from the spectra obtained from the measured samples, the energies of the involved peaks have to be determined by a Gaussian fit. These energies should be compared with the table of the emission lines (*Appendix A*) in order to identify the corresponding elements in the sample.

Some processes occurring when the emitted X-rays impact the detector may lead to additional peaks that are not to be taken into account in the actual fluorescence process in the sample. The XRF spectrum has thus to be corrected. Those parasite peaks are:

- ***Escape peaks***

When the X-rays interact in the detector, they undergo a complete photoelectric absorption. When the X-ray undergoes a photoelectric absorption by a Si atom, it emits a photoelectron and a Si characteristic X-ray (1.75 eV). For the main photo-peaks appearing in the XRF spectrum, both secondary particles are stopped in the detector so the full energy of the incident X-ray is finally detected. The escape peaks appear when some of these Si X-rays escape the detector. The deposited energy is then reduced: a E keV X-ray deposits only $E - 1.75$ keV. As a consequence, the spectrum will have an associated escape feature at a 1.75 keV lower energy.

- ***Sum peaks (Pile-up)***

This phenomenon occurs when two or more X-rays impact the detector virtually instantaneously. The pulse created and measured is the sum of the all these X-ray energies which will lead to a characteristic line which does not correspond to the actual element. The XRF spectrum may also suffer from the scattering background due to Compton and Rayleigh effects.

The bremsstrahlung produced by the x-ray tube may contribute as a continuum under the main peaks. In addition, since there are always various materials in the vicinity of the detector, X-rays will interact with these producing *environmental interferences*.

3.2.4. Quantitative analysis for some Euro coins.

The concentration of the identified elements in the sample can be calculated from the corresponding peaks intensities. Generally the integrated intensity of a given emission line is proportional to the corresponding element. However, the emission probability (fluorescence yield) has to be taken into account. The fluorescence yield in term of atomic number is given in figure 8. Here ω_k is the probability for k- emission lines, γ_l probability for l-lines and ω_M for M-lines.

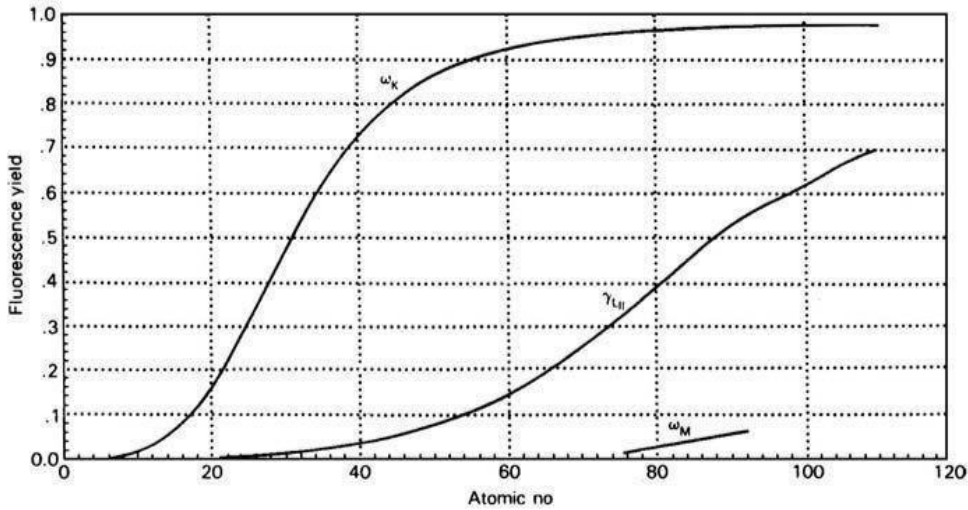


Figure 8: Fluorescence yield for all elements in term of atomic number. It tells the fluorescence emission probability for every line in every element.

For example, consider a sample with elements Ca(Z=20), Fe(Z=26) and Ni(Z=28). The integrated intensity of K-lines for these elements counted to I_{Ca} , I_{Fe} and I_{Ni} . To determine the concentrations of every element, first of all, these intensities must be normalized by multiplying each of them by the corresponding probability which can be extracted from the curve above.

The normalized intensities now equal to $I'_{Ca} = 0.15 I_{Ca}$, $I'_{Fe} = 0.3 I_{Fe}$ and $I'_{Ni} = 0.41 I_{Ni}$. After normalization, the concentration of element i can be calculated by the relation:

$$C_i = \frac{I'_i}{\sum_i I'_i}$$

Here I'_i is the normalized intensity of k-peak from element i , and $\sum_i I'_i$ is the sum of normalized intensities of all involved elements.

**Note: Error estimation should be associated with all calculations and results.*