

# Advanced Physics Laboratory

## XRF

### X-Ray Fluorescence: Energy-Dispersive analysis (EDXRF)

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## Contents

<b>1. INTRODUCTION.....</b>	<b>2</b>
<b>2. FUNDAMENTALS.....</b>	<b>2</b>
2.1 X-RAY PRODUCTION .....	2
2.1.1 <i>Continuous radiation</i> .....	3
2.1.2 <i>Characteristic radiation</i> .....	4
2.2 INTERACTION OF X-RAYS WITH MATTER .....	4
2.3 PRINCIPLE OF THE X-RAY FLUORESCENCE PROCESS .....	5
<b>3. QUALITATIVE AND QUANTITATIVE XRF ANALYSIS .....</b>	<b>7</b>
<b>4. EXPERIMENTAL SETUP .....</b>	<b>8</b>
4.1 THE X-RAY SOURCE .....	9
4.2 THE DETECTION/ACQUISITION SYSTEM .....	9
4.2.1 <i>Working principle of the SDD detector</i> .....	9
<b>5. OBJECTIVES AND TASKS.....</b>	<b>11</b>
<b>6. EXPERIMENTAL PROCEDURE.....</b>	<b>12</b>

## 1. Introduction

X-ray fluorescence (XRF) analysis is one of the most common non-destructive methods for qualitative as well as quantitative determination of elemental composition of materials. It is suitable for solids, liquids as well as powders. There are two main methodological techniques that are wavelength dispersive analysis (WD-XRF) and energy dispersive analysis (EDXRF) where the spectra are collected simultaneously in a wide energy range. The latter one we use in our experiment. In this case, the range of detectable materials covers all elements from Sodium (Na) to Uranium (U) and the concentration can range from 100% down to ppm. Detection limit depends upon the specific element and the sample matrix but in general heavier elements have higher detection limit.

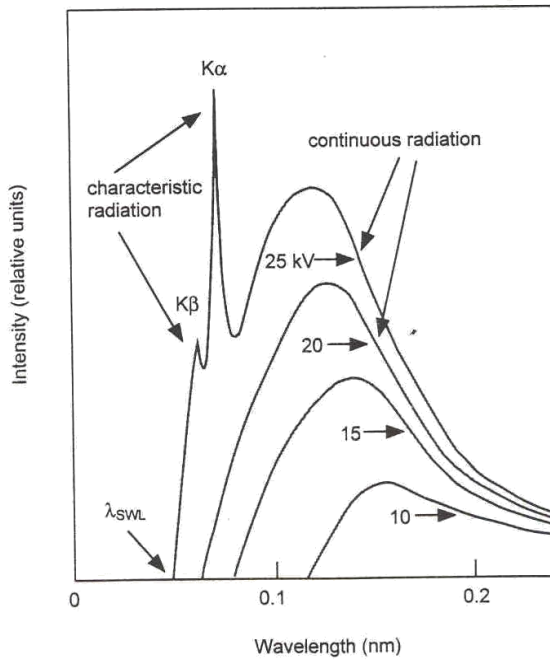
## 2. Fundamentals

### 2.1 X-ray production

X-rays cover the part of the electromagnetic spectrum between ultra-violet and gamma radiations. The characteristic wavelengths range from 0.1 to 100 Å corresponding to energies from 100 to 0.1 keV. Since their discovery by Wilhem Conrad Röntgen in 1895, X-rays have been widely used in many applications in medicine and technology. In research, due to their properties, they are extensively used in elemental and structural analysis.

X-rays can be produced by a radioactive source, an X-ray tube and by synchrotron radiation. In the present experiment, we use an X-ray tube. A typical X-ray tube is equipped with a heating filament (usually Tungsten) as a cathode. Due to Joules heating by the electrical current through the filament (glow emission) electrons are emitted and become accelerated in a high electric field towards an anode (target). X-rays are produced in the target. A typical emission spectrum obtained from an X-ray tube with a Molybdenum anode is shown in Figure 1 as a function of the applied voltages.

The spectrum is a superposition of a continuous part and characteristic lines (for 25 kV). The shape, the intensity and the maximum energy depend on the high voltage while the position of the discrete lines is characteristic of the anode material (as 1.54 Å for copper or 0.71 Å for molybdenum). The discrete lines appear only if the acceleration voltage exceeds a certain threshold (see below).



**Figure 1:** X-ray emission spectrum produced by an X-ray tube with a Mo anode, for different voltages.

### 2. 1. 1 Continuous radiation

The broad-wavelength band of radiation is called continuum also known as Bremsstrahlung (the German name for braking radiation). It arises due to deceleration of the accelerated electrons within the target material due to their interaction with electrons in the target element. The intensity distribution is characterized by a short wavelength limit ( $\lambda_{SWL}$  in Fig.1), it reaches its maximum at a wavelength 1.5 to 2 times greater than the minimum wavelength and it shifts towards shorter wavelengths with increasing voltage (Fig.1). The short wavelength limit corresponds to the particular case where the kinetic energy of accelerated electrons ( $eU$ ,  $U$  is the accelerating voltage) is entirely transformed into a photon energy and stopped:

$$E = h\nu = h \frac{c}{\lambda} = eU \quad (1),$$

where  $h$  is Planck's constant and  $c$  the velocity of the light. Thus, the short wavelength limit  $\lambda_{\min} = \lambda_{SWL}$  depends on the applied high voltage:

$$\lambda_{\min} [A^\circ] = \frac{hc}{eU} \approx \frac{12.4}{U[KV]} \quad (2)$$

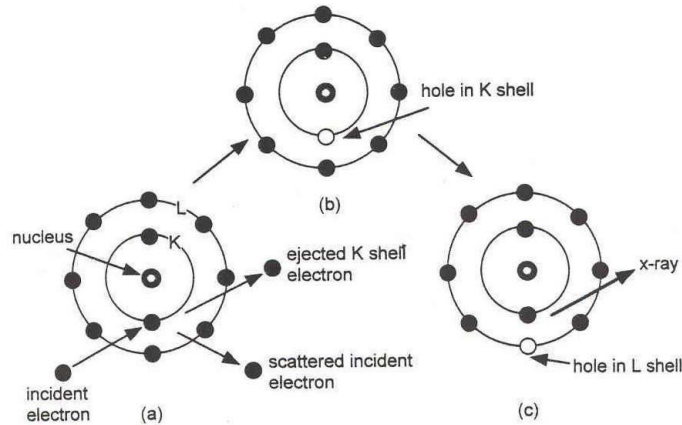
The distribution of the spectral continuum generated by the X-ray tube is given by Kramer's law:

$$I(\lambda) = K \left( \frac{\lambda}{\lambda_{\min}} - 1 \right) \frac{1}{\lambda^2} d\lambda$$

Where  $I(\lambda)d\lambda$  is the total intensity of the X-ray spectral continuum emitted in a wavelength range  $d\lambda$ ,  $K$  is a constant,  $i$  the beam current and  $Z$  the atomic number.

## 2. 1. 2 Characteristic radiation

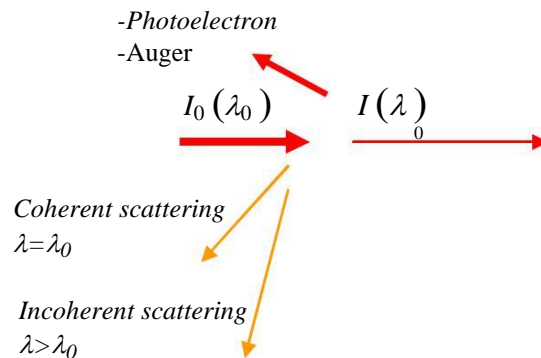
The energy of characteristic radiation equals the transition energy between two electron shells within an atom (typically between a higher shell with energy  $E_m$  and the K or L-shell with  $E_n$ ) appearing in the result of inner-shell ionization by the accelerated electron. The process of the inner-shell ionization and the subsequent X-ray emission is illustrated in Figure 2. The excitation/ionization can be performed in various electron levels and therefore the lines are named respectively.



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

## 2.2 Interaction of X-rays with matter

When a beam of X-ray photons like those produced from an X-ray tube falls onto a sample, a number of different processes may occur; as illustrated in Figure 3. The coming X-ray can either be absorbed (photoelectron effect, Auger effect) or scattered through the material with (Compton effect-*incoherent*) or without (Rayleigh effect-*coherent*) loss of energy.



**Figure 3:** Interaction of X-ray photons with matter

In the energy range smaller than 50keV photo-absorption is the main process. When photo-absorption occurs, only a certain fraction ( $I/I_0$ ) of the incident radiation 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-Beer's* equation:

$$I(\lambda_0) = I_0 \exp^{-(\mu\rho x)_a} \quad (3),$$

where  $x_a$  and  $\rho_a$  are the thickness and the density of the sample (absorber) respectively and  $\mu_a$  is the mass attenuation of the absorber for the wavelength  $\lambda_0$ .

### **2.3 Principle of the X-ray fluorescence process**

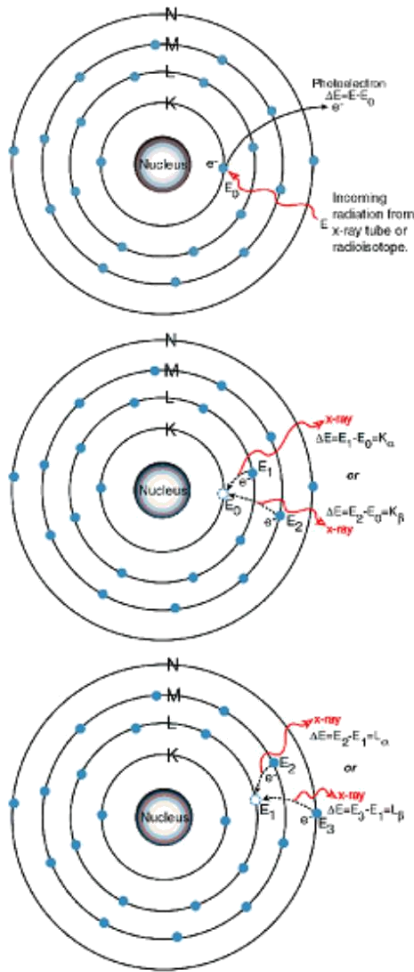
If the primary energy of X-rays is equal to or is larger than the binding energy of an inner shell electron it is likely that electrons will be ejected and consequently vacancies are created. The hole state has certain life time and becomes refilled again. The transition of the excited atom into a state with lower energy occurs via two competitive processes, the above mentioned *photoelectric* and *Auger* effects. In the photoelectric effect, the recombination is accompanied by a transfer of electrons from the outer shells with energy  $E_m$  into the inner shells with energy  $E_n$  filling the vacancies. This process induces the emission of a characteristic X-ray (fluorescence) photon with energy

$$h\nu = E_m - E_n \quad (4).$$

Therefore the energy of these secondary X-rays is the difference between the binding energies of the corresponding shells (Figure 4). The excited atom can also recombine by emission of *Auger* electrons, instead of characteristic X-rays, via the *Auger effect*.

The probability that characteristic X-rays will be emitted - and not an Auger electron- varies from one element to another and is described as the fluorescence yield. For elements of low atomic numbers, the Auger effect dominates, whereas emission of characteristic X-rays is more likely for heavy elements.

Each element has its unique characteristic energy spectrum (Fluorescence spectrum) composed by the allowed transitions of the specific atom in the result of X-ray excitation. XRF technique consists on the study of the produced characteristic spectrum. The XRF emission induced by photoelectron effect is shown in Figure 5 for an atom of titanium ( $Z=22$ ), whose K-shell electron acquires sufficient energy to escape from the atom.



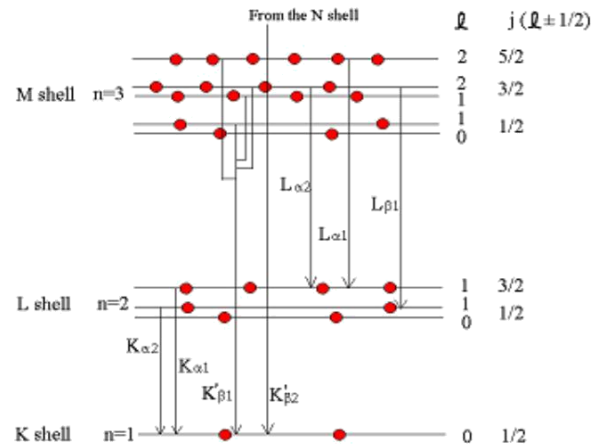
**Figure 4:** Ionization of the K-shell electron in the atom of Ti by photoelectron effect and emission of characteristic X-ray photons of different spectral series as a result of electron transition in the atom

The spectral lines appearing as a result of the above mentioned electron transitions are called *spectral series*. Transition to the K-shell form the K-series; transitions to the L-shells form the L-series, etc. The subscript Greek letter with a number ( $\alpha 1$ ,  $\beta 2$ ) denotes the atomic sub-shells participating in the electron transition (Fig. 4).

As mentioned before, the energy of the observed radiation is the unique fingerprint of a certain element independent of its chemical environment. 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:

$$E_{mn} = R_H (Z - \sigma)^2 \left( \frac{1}{n^2} - \frac{1}{m^2} \right) \quad (5)$$

Where  $R_H$  is the Rydberg constant,  $Z$  is the atomic number and  $\sigma$  is the screening constant of the atom. Every element has its own characteristic radiation that is its fingerprint. A table giving the energies of emitted photons for all elements of periodic table is giving in Appendix A.



**Figure 5:** Electron transitions and emitted spectral lines in the atom after the K-shell ionization

### 3. Qualitative and quantitative XRF analysis

#### Qualitative analysis

Based on Mosely's law, qualitative analysis is done using tabulated energy values of characteristic lines. The elements present in a sample can thus be identified from the energy of the peaks appearing in the spectrum. During the assignment of the XRF lines one must consider the fluorescence transition/selection rules and the fact that every element may be composed by a group of X-ray lines that have certain intensity relation. Also, the XRF spectrum can suffer from some parasite peaks being present in the XRF spectrum.

- *Selection rules*

The emission of the characteristic X-rays is governed by quantum mechanical selection rules:

- 1-  $\Delta n \geq 1$  where  $n$  is the principal quantum number
- 2-  $\Delta l = \pm 1$  where  $l$  is the angular quantum number
- 3-  $\Delta j = \pm 1$  where the quantum number  $J$  is the total momentum  $J=l+s$ ;  $s$  is the spin quantum number

Based on these rules, for the K series only  $p \rightarrow s$  transitions are allowed, yielding two lines for each principal level change. Similarly, vacancies in the  $l$  level give rise to  $l$  series lines which are more since  $p \rightarrow s$ ,  $s \rightarrow p$  and  $d \rightarrow p$  transitions are all allowed based on the above-mentioned selection rules.

- *Artifacts*

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 with the detector material, they undergo photoelectric absorption. In using silicon as detector material Si atoms emit photoelectrons and X-ray being characteristic for silicon ( $E_{mn} = 1.75$  eV) are emitted. 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. So any fluorescence peak at energy  $E$  is accompanied by an escape peak appearing with an energy  $(E-1.75)$  keV with respect to the fluorescence peak of any element.

#### Sum peaks (Pile-up) and background

Pile-up occurs when two or more X-ray photons impact the detector at a same time. The respective electron pulse created and measured is the sum of all these X-ray energies which will lead to a characteristic line with a multiple of energy of the true fluorescence energy of the probing 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*.

## Quantitative analysis

Once the line assignment is done, the peak intensity can provide the elemental concentration. Indeed, when a sample containing an element A is irradiated by a primary X-ray, the intensity of the generated fluorescent X-ray of element A is dependent on its fraction in the sample. The higher fraction of element A in the sample, results in a higher intensity of the fluorescent X-ray that is generated. Taking this into account, the volume fraction of certain element can be determined knowing the respective fluorescent X-ray intensity. In general, a quantitative XRF analysis can be conducted using two basic methods:

- The first one is to create a standard curve. This method involves measuring several samples with a known element concentration, and finding the relationship between the intensity of the measured element's fluorescent X-ray and the concentration. By referring this relationship, element concentration of unknown sample is obtained only with information on its fluorescent X-ray intensity.
- The other method is known as the fundamental parameter method and is based on theoretical calculation (FP method). Considering the type and properties of all elements that compose a sample the, intensity of each fluorescent X-ray can be derived theoretically. By utilizing this method, the composition of unknown sample can be extrapolated by its fluorescent X-ray intensity of each element.

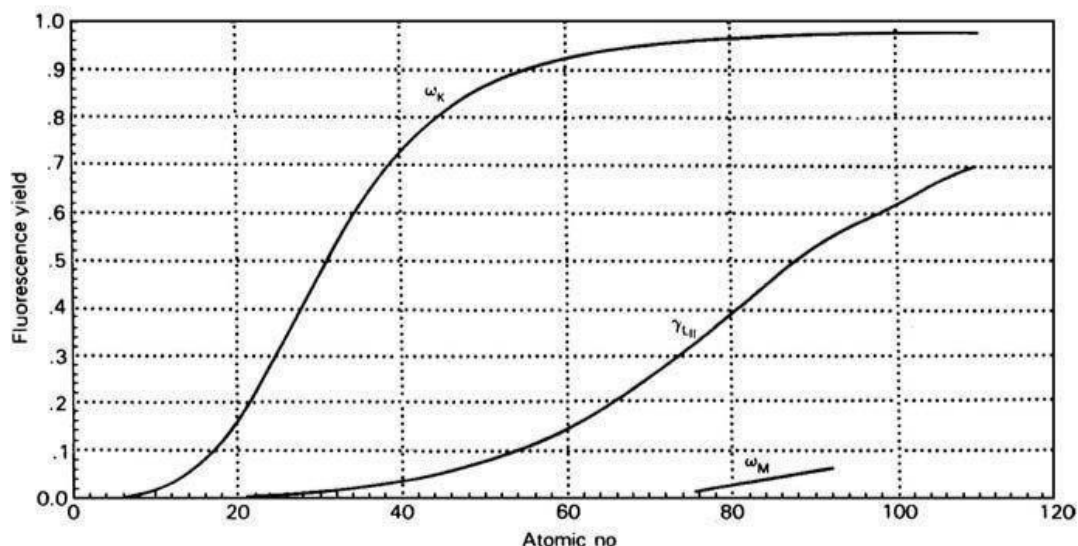
The characteristic lines intensities  $I$  in the spectra are proportional to the concentrations of the corresponding elements in the alloy material  $C$ . And hence, for a given alloy consists of elements  $a$ ,  $b$  and  $c$ , the relative concentrations are given by:

$$\frac{C_b}{C_a} \cong \frac{I_b}{I_a} \quad \text{and} \quad \frac{C_c}{C_a} \cong \frac{I_c}{I_a}$$

*or*

$$C_b = \left(\frac{I_b}{I_a}\right)C_a \quad \text{and} \quad C_c = \left(\frac{I_c}{I_a}\right)C_a$$

However, we have to take into account the probability of emissions of each line for each element. Graph below shows the fluorescence yield for each atomic number (for each element). This tells the probability of characteristic line emissions.





For example, consider element **a** as a reference element in the alloy material, the total concentration of the elements should be 100%, and thus, we get the following equation:

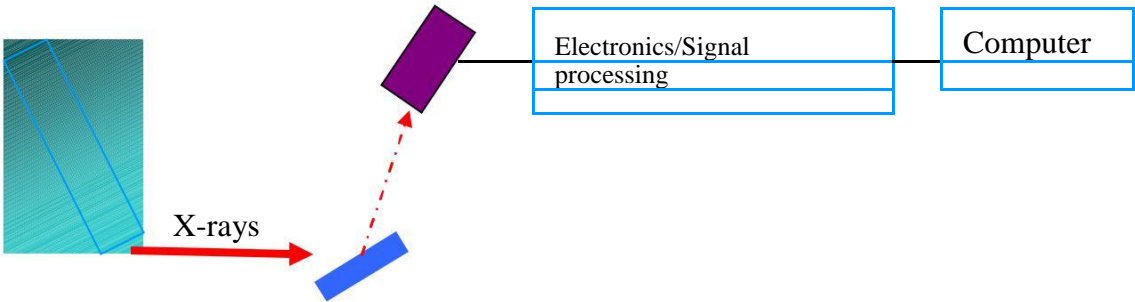
$$C_{a+} \alpha C_{b+} \beta C_c = 100\%$$

$$X + \alpha \left(\frac{I_b}{I_a}\right) X + \beta \left(\frac{I_b}{I_a}\right) X = 100\%$$

Where  $X = C_a$ .  $\alpha$  and  $\beta$  are the emission probability of K- $\alpha$  for elements **b** and **c** relative to element **a** which can be determined from the graph above. Once this equation is solved to find  $X$ , the concentration of element **a**, other concentrations could be found.

#### 4. Experimental setup

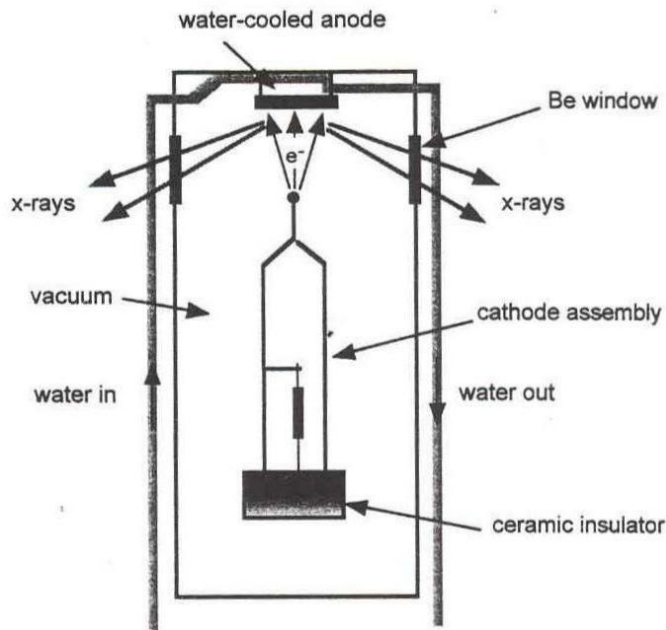
Figure 6 shows the arrangement of a typical X-ray fluorescence spectroscopy experiment which includes a source of primary radiation (an X-ray tube in our case), the sample whose X-ray spectrum is studied and an equipment to detect the secondary X-rays (X-ray detector) and to acquire and record the spectrum (acquisition and processing system).



**Figure 6:** Scheme of the arrangement of the experimental setup for X-ray fluorescence spectroscopy.

## 4.1 The X-ray source

The X-ray tube used in our experiment provides a minimum current of 5 mA with a energy of 8 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 that certain X-rays can escape the shielded X-ray tube towards the sample.



**Figure7:** Schematic of the main components of an X-ray tube

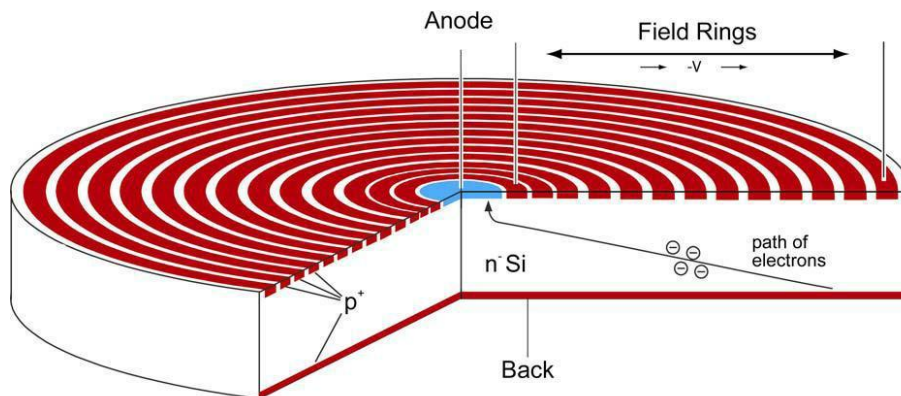
## 4. 2 The detection/acquisition system

### 4. 2. 1 Working principle of the SDD detector

The basic principle of an energy dispersive detector in general is that each detected photon creates an electric pulse with amplitude proportional to the photon energy.

The Silicon drift detector (SDD) used in this experiment was introduced by Gatti and Rehak in 1984. It consists of a volume of fully depleted silicon in which an X-ray photon generates an electron-hole pair. Due to the electric field the electrons will “drift” towards a small sized collecting anode to generate a signal pulse as shown in figure 8. One side of the detector is covered by a number of increasingly reverse biased field rings (concentric electrodes) generating the drift field. The entrance side for radiation is the non structured p+-junction denoted in the figure as *back* contact, giving a homogeneous sensitivity over the whole detector area. 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).

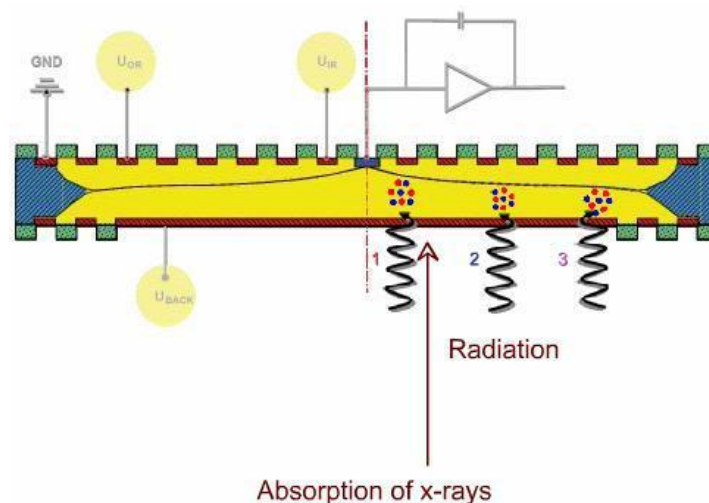


**Figure 8:** Scheme of the Silicon Drift Detector (SDD)

The 'drift' concept of the SDD allows for throughput beyond 10,000 counts per second (CPS). This high counting rate is insured by the signal collection in the middle of the system on a small anode which induces a small electrical capacity. Another consequence is a better energy resolution and shorter collection times compared to other X-ray detectors.

Working principle of the SDD detector

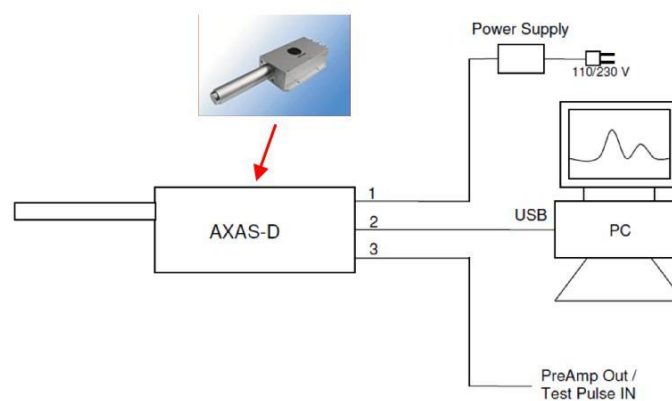
Like other solid state x-ray detectors, SDD detectors measure the energy of an incoming photon by the number of electron-hole pair generated in the detector material. Figure 9 sketches the working principle of such detector.



**Figure 9:** Working principle of a SDD detector

When a photon hits the detector (back side), it creates pairs of electron-hole pairs which are separated within the electric field. The holes travel to the electrodes (back) and the electrons are forced by the ring electrodes to drift towards the anode. The collection of the electrons at the anode depends on their rise time. Slower electrons have to drift a longer path before reaching the anode.

The electric signal produced by the detector is sent to an electronic board for signal processing. It is first amplified by a preamplifier. Then, the current pulses generated by the SDD are translated into *counts* (counts per seconds CPS) and segregated into channels according to energy via an MCA (Multichannel Analyser).



**Figure 10:** Connection overview of the KETEK AXAS-D

The detector used in this experiment is a KETEK VETUS SDD detector with an active area of  $7 \text{ mm}^2$  and a  $12.5 \text{ }\mu\text{m}$  Beryllium window. The SDD detector is optimized to detect photons in the energy range from  $1 \text{ eV}$  to about  $20 \text{ keV}$ .

The KETEK SDD is housed into a so called Analytical X-ray Acquisition System-Digital (AXAS-D) which includes also the preamplifier, the MCA as well as the Digital Pulse Processor (DPP) and a cooler system. Such a compact detection/acquisition system can be plugged directly via a USB to a PC and it only needs an external power supply as indicated in figure 10. For the acquisition of the spectra the software MCDWin is used.

## 5. Objectives and tasks

The purpose of this laboratory work is to study the production of fluorescent X-rays in a solid sample by means of primary X-rays, emitted by the x-ray tube. The acquired XRF spectra will be interpreted in terms of qualitative and (semi)quantitative analysis

The main tasks are:

- Energy calibration of the SDD detector

- Identification of characteristic lines from the X-ray tube.
- Qualitative and (semi)quantitative identification of the chemical composition of an alloyed material.
- Qualitative and (semi) quantitative analysis of the XRF spectra acquired from some Euro coins.
- Estimation of the errors.

## 6. Experimental procedure

### Start up procedure

- Connect external power supply (+/-12V) to AXAS-D
- Connect AXAS-D to USB port of your running PC-System
- Open the file “DPP.exe” by double clicking the DPP icon on the desktop: The DPP is connected to your PC-System. Two windows are opened: DPP Server and MCDWin.
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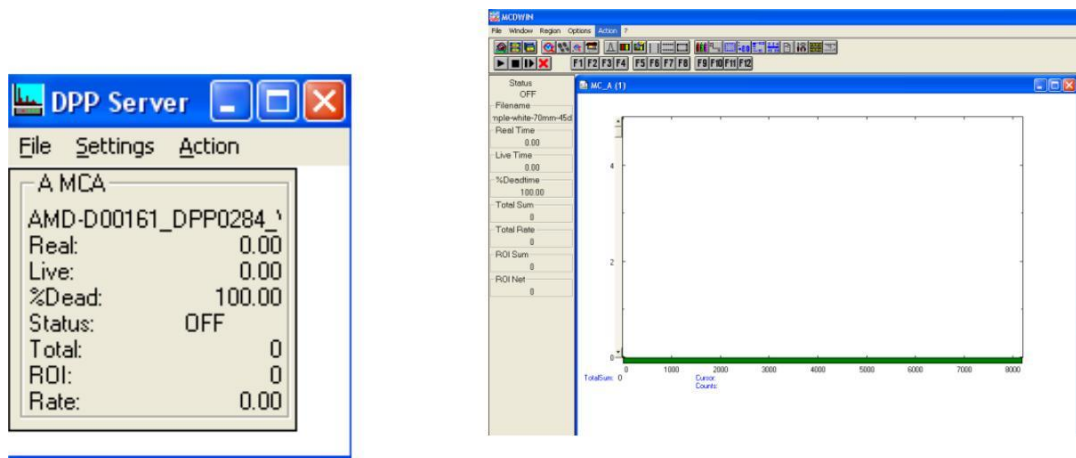



Figure 11: DPP Server and MCDWIN window

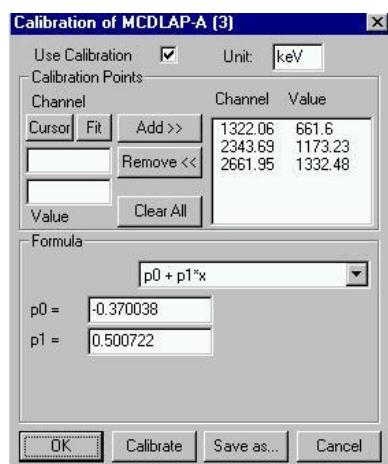
## Energy calibration of the SDD detector

This will be done with the aid of the characteristic radiation of a multi-elements standard sample.

Procedure:

- Put the sample on the sample holder, orient it with an angle of 45°.
  - Close the X-ray machine
  - Open the shutter (press E) to open the window of the X-ray tube.
  - Set *progressively* the filament voltage to **40 kV** and then the current to **20 mA**.
  - Use the **Action** Menu or the **Start** toolbar icon to start the acquisition of the XRF spectrum from the sample. Set the counting time to 200 sec (by using the **Range, Preset** icon  ).
- When you save the acquired spectrum, 2 files are created: a header file (extension \*.mcd) as well as an ASCUI file.

Use the Calibration Menu item or the corresponding icon to open the Calibration dialog box.



**Figure 12:** Calibration dialog box

The elements contained in the investigated sample are: Fe, Cu, Mo, Pb and Sn. By using the energy values of the characteristic lines corresponding to each element (Annexe A) identify the different characteristic lines corresponding to the different elements and assign each channel number to an energy value in the calibration dialog box. Choose one of the calibration formulas and then click on “calibrate”. The chosen calibration can be saved as a control file (\*.CTL) to be loaded in order to read XRF spectra as a function of energy. Check “use calibration” in the *Axis Parameters* dialog box to switch to the energy axis (use the “Axis options” icon). To perform accurate calibration, you should create a region of interest (ROI) for each of the chosen characteristic lines and then use the Gaussian fit.

### X-ray fluorescence from an X-ray tube

1. Acquire the XRF spectrum from the X-ray tube and calibrate it using the calibration file already chosen using the reference sample. Identify the different characteristic lines and eventually parasite peaks (escape peaks,...). Which material is used as anode in the X-ray tube you have used? Explain why the characteristic lines can be observed only for high voltage above 20 kV as shown in Figure1?

### X-ray fluorescence from an alloyed material

2. Record the XRF spectra from the three samples (yellow, white and red) consisting of two pure metals and one corresponding alloy.
3. Identify all the lines observed in the acquired XRF spectra from each target. What is the chemical composition of each sample? Which alloyed material have you investigated?
4. By using a semi-quantitative analysis determine the concentration of each element within the alloy. Discuss your results.

### X-ray fluorescence from some Euro coins

5. Identify all the lines observed in the acquired XRF spectra from Euro coins of *5 cent* and *2 Euro* respectively. What is the chemical composition of each target? Compare your results to the compositions values published. Discuss your results.

### **Literature**

- **X-ray Techniques: Overview** *Ron Jenkin* in “*Encyclopedia of Analytical Chemistry*”  
R.A. Meyers (Ed.) pp. 13269–13288, Ó John Wiley & Sons Ltd, Chichester, 2000
- [http://en.wikipedia.org/wiki/X-Ray\\_fluorescence](http://en.wikipedia.org/wiki/X-Ray_fluorescence)