Development and optimization of scanning micro-XRF instrumentation using monochromatic excitation

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List of Abbreviations

ADC  Analog to digital converter
BAS  Baseline average sample
cps  Counts per second
DT   Dead time
FWHM Full width at half maximum
ICR  Incoming count rate
JFET Junction gated field-effect transistor
NIST National institute of standards and technology
MCA  Multichannel analyze
MDL  Minimum detection limit
MGT  Minimum gap time
LT   Live time
OCR  Outgoing count rate
PT   Peaking time
RT   Real time
SDD  Silicon drift detector
SRM  Standard reference material
ST   Shaping time
XRF  X-ray fluorescence
Chapter 1: Introduction and Outline

Recently, the Ghent University X-ray Microspectroscopy and Imaging research group has developed a new scanning micro-XRF instrument, called the MicroXRF. It is unique in its kind as it is based on monochromatic, focused beam excitation for elemental analysis on the microscopic scale. The instrument combines an advanced energy-dispersive detector with a state-of-the-art monochromatic X-ray source. The energy-dispersive detector used is a silicon drift detector, characterized by its good energy resolution even at high count rate. The X-ray source is a molybdenum-tube, with integrated doubly curved crystals to monochromatize the beam. The benefit of using monochromatic excitation is the dramatically reduced scatter background, resulting in (1) much higher signal to background ratios in the measured XRF-spectra, and (2) the easier quantification due to the elimination of uncertainties associated with the polychromatic energy-distribution of the incident beam. The sample can be mounted on a stage with positioning system, which move in the X-,Y-,Z- or θ-direction. This enables the use of performing point measurements, line scans, mappings or even a tomography.

The goal of this thesis is to optimize the detector parameters of the MicroXRF instrument, i.e., to find the optimal detector settings for automated routine measurements. In order to achieve this goal, the influence of the different detector parameters on the quality of the acquired XRF spectra was investigated and can be described in terms of energy resolution, dead time, minimum detection limits and XRF spectral response.

The outline of the thesis is as follows. Chapter 2 gives an overview on the general principles of X-ray fluorescence spectroscopy, the discovery and special properties of X-rays and its interaction with matter. A general explanation is given about the sources and detectors used in X-ray fluorescence spectroscopy in Chapter 3. The Mo-tube with the doubly curved crystals and the silicon drift detector are explained in more detail. The electronic chain the detected signal undergoes by the digital pulse processor is described in Chapter 4, a definition and explanation of all the parameters used to optimize the detector is provided.
Chapter 5 describes the experimental setup and the characteristics of the MicroXRF instrument, the spectrometer used to collect all XRF spectral data provided in this master thesis. All results with respect to the detector optimization are summarized in Chapter 6. Each section focuses on a given detector parameter describing its influence on the spectrum and on other detector parameters. The detector parameters are investigated by (1) using the Prospect software (version 1.0.x, XIA LLC), which shows the waveforms of the signal received by the preamplifier or analog to digital converter, or (2) by analyzing the spectrum itself, deriving the detector dead time, energy resolution and minimum detection limits. Finally, a conclusion concerning the optimal detector parameters for automated routine measurements is formulated in the last chapter.
Chapter 2: XRF Principles

2.1 Definition and Discovery of X-rays

X-rays are part of the electromagnetic spectrum, with energies between 0.1 and 100 keV, which approximately correspond to a wavelength range of 0.01 to 10 nm (Figure 2-1).

![Electromagnetic Spectrum Diagram]

X-rays were discovered in November, 1895 by Wilhelm Conrad Röntgen, a professor in Munich, who encountered visible fluorescence originating from a barium platinocyanide screen induced by an unknown type of radiation. He called this unknown radiation X-rays, referring to its unknown origin. It became quickly clear that these unknown rays could penetrate through optically non-transparent objects, making it possible to visualize e.g. brass weights within a closed wooden box or to see the bones when irradiating a human hand. His discovery was awarded with the first Nobel prize in Physics in 1901, before the actual nature of X-rays was established. Röntgen’s early experiments not only established the foundations of medical imaging using X-rays but also drew a tremendous interest in other scientific disciplines and now X-rays are widely used in the world of science.

Nowadays, it is known that X-rays are electromagnetic radiation. They exhibit a particle-wave duality. Properties like polarization, interference and diffraction can be explained by
the wave-nature of the electromagnetic radiation. On the other hand, the photoelectric effect (see section 2.2.1) can only be explained due to their particle nature. X-rays have a highly penetrating character, which is dependent on the energy. High energy radiation will penetrate the material deeper than low energy.

The second most important discovery with respect to the foundations of X-ray fluorescence spectroscopy was made by Moseley, who demonstrated that there was a strict relation between the energy of the emitted X-ray fluorescence radiation by excited atoms and the atomic number of chemical elements (Figure 2-2). When the atomic number was plotted versus the square root of emission frequency, a straight line was followed. This well-defined relationship between atomic numbers and emission frequencies/energies/wavelengths of the characteristic X-ray lines emitted by atoms as a result of X-ray based excitation constitutes the basis of elemental analysis by XRF spectroscopy.

Figure 2-2: Moseley’s relation: linear relation between the atomic number and the square root of the X-ray emission frequency[3].
2.2 Interaction with Matter

When an X-ray photon interacts with matter, several processes can occur within the energy range of 0.1-100 keV. A first type of interaction is the photo-electric effect. A photon is absorbed, ejecting an inner shell electron from the atom. A second type of interactions are scattering effects, a difference is made between elastic and inelastic interaction, referred to as Rayleigh and Compton scattering. A given photon can also pass through matter without any interactions. This occurs with a higher probability at high energies and within thin samples. Other effects that can take place in the MeV energy range are photonuclear absorption and pair production. Since these effects will not occur in the 0.1 to 100 keV range, they will not be addressed in this thesis.

2.2.1 Photoelectric Effect

During the photoelectric effect a photon is absorbed and its energy is fully transferred to an inner shell electron, which is ejected from the atom (Figure 2-3 left). The kinetic energy of the ejected electron is described by:

\[ E_e = h\nu - E_b \]  \hspace{1cm} (2-1)

Where \( h \) is the Planck constant, \( \nu \) the frequency of the incoming photon and \( E_b \) the binding energy of the ejected electron. In order to eject an electron, the energy of the incoming photon should be higher than the binding energy of the electron.

When the electron is ejected, an inner shell vacancy is created in the atom. This can be filled as a result of an electron transition from a higher shell (Figure 2-3 right). During this process excess energy is released either in the form of a characteristic X-ray, a fluorescent X-ray photon, or in the form of a so-called Auger electron. The fluorescence photon is called a characteristic X-ray, because the energy of the photon is equal to the difference between the energy levels of the shells involved in the transition. Each shell has a characteristic energy for a given atom (apart from subtle shifts due to molecular effects), so that the difference between two shells is also characteristic for a certain element.
Figure 2-3: Photoelectric effect: an X-ray photon is absorbed by an atom and a photoelectron is ejected (left); the filling of an inner shell vacancy by an outer shell electron\textsuperscript{[5]}.

The alternative relaxation process of an excited atom after the photoelectric effect is coupled with the ejection of the so-called Auger electron. The kinetic energy of the Auger electron corresponds to the difference between the energy of the initial electron transition and the ionization energy of the shell where the Auger electron originates from. In XRF measurements the emission of an Auger electron is undesirable since this represents a radiationless relaxation of the atom. The X-ray fluorescence emission and the emission of Auger electrons are competing processes, where the probability of the Auger effect is higher for low Z elements. This is one of the fundamental reasons that make low Z elements more difficult to detect in XRF. In case of higher atomic numbers, the probability of fluorescence emission is dominant. Other radiationless transitions are the so-called Coster-Krönig transitions. In this case electrons undergo transitions within sub-shells of the same shell, for example by an L\textsubscript{3}-L\textsubscript{1} transition.

The chance an X-ray will interact with matter according to the photoelectric effect is given by the photoelectric cross-section \( \tau \). If the interaction of a photon caused a vacancy, the atom has a probability to relax due to X-ray fluorescence or Auger electron emission. The probability it relaxes due to fluorescence is given by the fluorescent yield \( \omega \), which is specific for each shell and atom.
2.2.2 Scattering Effects

An X-ray photon can be scattered by electrons in the atom. There are two types of scattering processes, referred to as elastic or inelastic scattering (Figure 2-4). When a photon is scattered elastically by an atomic electron, it loses no energy, only the direction of photon propagation will change. The elastic scattering process by atomic electrons is also called Rayleigh scattering, which has a higher relative probability in case of heavier atoms and with low energy X-rays.

![Figure 2-4: Schematic overview of Compton (left) and Rayleigh (right) scattering][9].

The other scattering type is the so-called inelastic or Compton scattering process. During the (atomic) Compton scattering a photon collides with a bound atomic electron, losing a part of its energy. The photon changes its direction of propagation, losing a certain amount of energy which is transferred to the so-called Compton electron. The remaining energy of the photon is given by the equation:

\[ E_{\text{Compton}} = \frac{E_0}{1 + \frac{E_0}{m_e c^2} (1 - \cos \theta)} \]  

(2-2)

With \( E_0 \) the incident energy, \( \theta \) the scattering angle, \( c \) the speed of light in vacuum and \( m_e \) the rest mass of the electron. Because the Compton-electron is ejected from the atom, this process will occur mainly with electrons in the outer shells of the atom. The electrons in these shells have lower binding energies than the ones in an inner shell. Compton scattering
has a higher probability to occur with lighter elements and gives information about physical parameters such as electron density, target mass and mass thickness \(^{[11]}\). The ratio between the Compton scatter intensity and the Rayleigh scatter intensity gives information about the mean atomic number of the matrix \(^{[12]}\). To calculate the Rayleigh and Compton scatter probabilities, one needs to use the so-called scattering cross-sections \(\sigma_R(E,Z)\) and \(\sigma_c(E,Z)\), which are the function of both atomic number \((Z)\) and X-ray energy \((E)\). One can describe the angular dependence of the Rayleigh and Compton scattering processes through the use of differential scattering cross-sections, as defined below:

\[
\frac{d\sigma_R}{d\Omega}(\theta, \phi, E) = \frac{r_e^2}{2} \left[ 2 - \sin^2 \theta (1 - p + 2p \cos^2 \phi) \right] F^2(x, Z) \tag{2-3}
\]

\[
\frac{d\sigma_c}{d\Omega}(\theta, \phi, E) = \frac{r_e^2}{2} \left( \frac{E}{E_0} \right)^2 \left[ \frac{E}{E_0} + \frac{E_0}{E} - \sin^2 \theta (1 - p + 2p \cos^2 \phi) \right] S(x, Z) \tag{2-4}
\]

Here is \(\theta\) the scattering angle between the incoming beam and the X-rays scattered towards the detector, \(\phi\) is the angle between the detector axis and the plane of polarization, \(E\) is the energy of the scattered photon, \(E_0\) is the energy of the incoming photon, \(r_e\) is the classical electron radius, \(p\) is the degree of linear polarization, \(F(x, Z)\) is the atomic form factor and \(S(x, Z)\) is the incoherent scattering function, both are functions of the atomic number and the variable \(x = \frac{\sin(\theta)}{\lambda} \left[ \AA^{-1} \right]\). Both values can be found in databases \(^{[6]}[7]\).
3.1 X-ray Tube and Focusing Optics

The most conventionally used sources in laboratory X-ray spectroscopy are X-ray tubes. Other types with wide applications are the synchrotron-based sources or radio-isotopes. To make an X-ray source monochromatic, several types of monochromators can be used. In this work only the combination of a molybdenum X-ray tube with a doubly curved crystal optics is described, which serves as a monochromator and X-ray focusing device simultaneously.

3.1.1 X-ray Tube

X-ray tubes are evolved from Crookes’ Cathode Ray Tubes, invented in the late 19\textsuperscript{th} century. The X-ray tube, shown in Figure 3-1, consists of a tungsten filament cathode and a target anode. The anode is a thin layer of pure metal (e.g. Mo, Rh, Pd, ...). A high voltage is applied between the cathode and the anode. Electrons generated from the heated cathode accelerate to the anode under the influence of the applied electric field. The electrons collide at high speed with the target material (anode) and, next to heat, generate X-rays.

![Diagram of an X-ray tube](image)

Figure 3-1: Working principle of an X-ray tube\textsuperscript{[13]}. 

\textsuperscript{[13]}
There are two effects which contribute to the generated X-ray radiation. When an electron collides with the target atoms, it will eject electrons from the material via impact ionization, generating inner-shell vacancies. Electrons from higher shells will fill the vacancies releasing energy in form of characteristic X-rays. This is a process similar to the photoelectric/fluorescence effect described earlier. This process results in X-ray radiation at specific energies, characteristic for the target anode, due to the transition of outer shell electrons into vacancies generated in the inner shells. This are the discrete components of the X-ray emission spectrum from an X-ray tube, exhibiting Mo-K and Mo-L emission lines in case of a Mo-tube. A second type of X-ray radiation, corresponding to the emission of a polychromatic spectral component in the tube spectrum, is called Bremsstrahlung. The process gives rise to a continuous spectrum. When electrons collide with the anode material, they will penetrate the material and are decelerated. During the deceleration of the electrons, or charged particles in general, some of their energy is converted into X-rays, known as ‘braking radiation’ or Bremsstrahlung. This has a continuous energy distribution with a maximum energy defined by the applied tube voltage. Therefore X-ray tubes are not monochromatic, but emit a continuous, polychromatic spectrum. As mentioned earlier, not all the energy of the electron is converted to radiation. The major part of the energy of the electron is lost as heat when it interacts with the anode material. Therefore it is necessary to cool down the system with air or water to prevent the melting of the anode. The X-rays leave the tube through a beryllium window, which forms the barrier between the vacuum inside the tube and the surrounding atmosphere. Because the vacuum inside puts a great force on the barrier, the beryllium window must be strong enough to withstand this force. A thin Beryllium window is not only sufficiently strong to withstand the pressure difference, but being a low Z material, it will only absorb the very low energy X-rays\textsuperscript{[10]}.

3.1.2 X-ray Optics: Doubly Curved Crystals

In order to produce a monochromatic and focused X-ray beam, the beam is two-dimensionally focused by diffraction optics integrated in the Mo-tube, based on a toroidally curved crystal. The benefit of using monochromatic instead of polychromatic excitation is the improved sensitivity through reduced background and simpler quantitative analysis.
Monochromat
ic excitation eliminates the X-ray scattering background under the fluorescent peaks, since the continuous Bremsstrahlung component of the tube-spectrum generated by the electron bombardment is eliminated by the diffraction optics, which gives an improved sensitivity\textsuperscript{[14][15]}. Singly curved crystals are used to provide line focusing from a point source. Two-dimensional focusing geometries can be achieved by the Johann or Johannson geometry. The Johannson geometry provides a larger collection angle but is difficult to achieve in practice. Three-dimensional focusing geometries are obtained by rotating the Johann or Johannson geometry about the source-image line\textsuperscript{[17]}. Figure 3-2 shows the geometry of a Johann doubly curved crystal. S is the source location, I the image location, R the radius of the focal circle, φ the rotating angle and θ\textsubscript{B} the Bragg angle.

![Figure 3-2: Geometry of a Johann type DCC\textsuperscript{[14]}.

The incoming polychromatic beam travels from point S to the bended crystal. The crystal will only diffract a narrow band of the X-ray beam spectrum, when they fulfill the Bragg condition. Equation 3-1 gives Bragg’s law, with λ the wavelength of the incident beam, d the distance between two planes of the lattice and θ the angle between the incident beam and the scattering plane:

\[ n\lambda = 2dsin\theta \]  

(3-1)

The diffracted beam is focused on point I. The focal spot size is dependent of the spot size of the X-ray source and the reflection efficiency is affected by the shape of the crystal surface. The diffraction crystal material is made from mica or silica. When the crystal has imperfections, it has a decreased reflection efficiency and the focal spot of the reflected beam is broadened.
3.2 Energy-dispersive X-ray Detectors

One of the possibilities for X-ray detection has been established more than 100 years ago by Wilhelm Conrad Röntgen during his discovery of X-rays, when he observed visible fluorescence from a barium platinocyanide screen upon the impact of X-rays. The detection with fluorescent screens is not energy-dispersive, only the presence of X-ray illumination is detected. To get an energy-dispersive detection, the X-ray photon energies should be measured simultaneously with the detection, which can be achieved by semiconductor detectors. Another way to detect X-rays is by using a wavelength-dispersive detector, based on the use of analyzer crystals, which provides a much better energy resolution. Because the energy-dispersive detector has a wider range of application, as it can detect different elements simultaneously, this type of detectors are used in mainstream XRF spectroscopy\(^1\). There are different types of energy-dispersive detectors depending on the used semiconductor material and structure. The MicroXRF instrument uses a so-called silicon drift detector (SDD) which is described in detail.

3.2.1 General Information

**Basic Principle**

A detector is used to convert the energy of a photon, released by interacting with the detector material, into an electric signal. This signal is processed by digital filters to filter out the noise and get out a signal with the best signal to noise ratio.

When an X-ray photon interacts with the active crystal of a detector, it mainly undergoes absorption by the photo-electric effect depending on the energy of the photon and detector material. The produced high energy photoelectron dissipates its energy through a series of interactions that promote valence-band electrons to the conduction band. In case of the X-ray energies involved, a large number of electron-hole pairs are formed correlated with the dissipated energy. Mostly an average of 3.6 eV is dissipated when an electron-hole pair is created in the Si detector material\(^1\). The generated charge-carriers are collected by the high-voltage bias diode generating an electric pulse. The total charge collected is
proportional to the total energy of the X-ray photon, which can be derived from the measured pulses\(^1\)[19].

Figure 3-3: Working principle of an energy-dispersive detector\(^3\).

Whenever the detector detects an X-ray photon, it needs some time to analyze and process the signal. Within this period, called the dead time, no other X-ray photons can be detected. A difference needs to be made between the time of a measurement, the real time (RT), and the time the detector actually detects X-ray photons, the live time (LT). The dead time (DT) can be calculated in two different ways:

\[
DT (\%) = 100 \times \frac{LT - RT}{LT}
\]

(3-2)

\[
DT (\%) = 100 \times \frac{ICR - OCR}{ICR}
\]

(3-3)

With the ICR as the incoming count rate, the X-ray photons that enter the detector per second and the OCR as the outgoing count rate, the X-ray photons that actually have been processed per second.

**Detector Artifacts**

When detecting an X-ray photon, it is possible that not the full energy of the incident photon is registered. This results in detector artifacts in the obtained spectrum. A first type of artifact is called an ‘escape peak’ which can be observed when an X-ray fluorescent photon generated within the active material of the detector (in our case Si) escapes from the
detector material without further interactions. This means that the registered energy will be $E'$ lower than the energy of the incident photon, where $E'$ corresponds to energy of the fluorescent photon. When the active material of the detector is Si, the most probable escape energy $E'$ corresponds to the energy of the Si-K$_\alpha$ fluorescent line, i.e. 1.7398 keV. In an XRF spectrum, the escape peaks can be identified by comparing the low-energy escape peaks with the true XRF peaks, which will have a difference in energy of $E'$. This can be shown in Figure 3-4, the energy of the escape peak is 1.7398 keV lower than the energy of the Fe-K$_\alpha$ peak.

The second type of an artifact that can be observed in a typical XRF spectrum is called a sum-peak. When two photons enter the detector at nearly the same time, they will both create electron-hole pairs. When the electronics signal read-out or processing is too slow, it cannot distinguish between the two photons, and processes them as a single signal. This causes the appearance of the so-called ‘sum-peak’ in the detected XRF spectrum, which can be observed at the sum of the energies of the two incident photons, as seen in Figure 3-4 for the iron peaks. Ways to reduce the occurrence of sum peaks are using a detector with faster read-out and processing speeds or reduce the number of photons that reach the detector. The beam intensity can be reduced by using absorbers or filters.

![Figure 3-4: XRF spectrum of an iron foil showing the detector artifacts: escape peak and sum-peaks.](image)
Detector Energy Resolution

An energy-dispersive detector measures the energy distribution of the detected X-ray photons, corresponding to the XRF-spectrum. The energy resolution expresses the separation efficiency of two peaks in the spectrum. Because of the non-zero detector noise and statistical fluctuations in the generated electron-hole pairs, the peak at a given X-ray photon energy will not be a narrow line. Instead, the detected XRF-lines appear in the detected spectrum as relatively broad, Gaussian-like peaks. To express the energy resolution defined by a Gaussian peak, its Full Width at Half Maximum (FWHM) is determined. The higher the FWHM (corresponding to lower resolution), the more difficult it is to make a clear distinction between two neighboring peaks. The resolution (FWHM) of a semiconductor ED-detector equation at a given energy \( E \) can be expressed as follows \(^{[1]} \):

\[
FWHM = 2.35 \sqrt{\frac{F \varepsilon E}{N}} + N
\]  

(3-4)

where \( F \) is the Fano factor, \( \varepsilon \) a conversion factor from energy to the number of charge carriers, \( E \) the energy of the X-ray fluorescent line, \( N \) the noise in the spectrum. A typical value for the Fano factor for Si-based detectors is 0.115 eV. This factor is introduced to correct an error introduced by the Poisson statistics with semiconductor detectors. The conversion factor for one charge carrier in a Si-based detector is 3.6 eV \(^{[1]} \).

When considering X-ray fluorescence spectroscopy, the detector resolution is a function of the energy. A higher energy photon will result in a higher number of generated charge carriers, which introduces a higher statistical uncertainty. This is one of the reasons that the FWHM increases towards higher energies.

Within this thesis, the energy resolution with its standard error is calculated using in-house software.

Minimum Detection Limit

The minimum detection limit (MDL) describes the minimum concentration of an element that needs to be present in the analyzed sample in order to be detectable with a given statistical certainty, and thus a very important figure of merit for an analytical instrument. A
MDL value for a given element is expressed as a concentration, either relative written as weight percent or parts per million (ppm) or absolute as a quantity in the order of µg or moles. The following equation is used to determine the relative MDL in XRF spectroscopy \(^{[10]}\):

\[
C = \frac{3\sqrt{N_{b,i}}}{N_{p,i}} C_i
\]  

(3-5)

In this equation \(N_{b,i}\) stands for the counts of the background under the most intense fluorescent line of element \(i\), \(N_{p,i}\) stands for the counts in its XRF peak and \(C_i\) is the concentration of the element of interest. Standard Reference Materials (SRM) produced by NIST\(^{[18]}\) with well documented concentrations of detectable elements are typically used to calculate the achievable minimum detection limits for given detector/instrumental settings. Different parameters have an influence on the MDL, including the atomic number of the element of interest, the matrix of the sample and the time of measurement. The minimum detection limit is strongly element dependent: low Z elements have a lower fluorescence yield and suffer considerably from absorption effects in the sample matrix, in the surrounding air and in the detector window, therefore a much higher MDL is obtained compared with elements having higher atomic numbers. Since the matrix of the sample attenuates the signal of the target element(s), therefore different MDL values are obtained for samples having different matrices. The MDL values are also functions of the measuring time: the detection limits are inversely proportional with the square-root of the data-collection time.

Within this thesis, the MDL with its standard error is calculated using in-house software.

### 3.2.2 Silicon Drift Detector

In 1984, Gatti and Rehak introduced the silicon drift detector \(^{[27]}\), which is becoming the most frequently used XRF-detector type in the energy range of 1-30 keV. It was first designed for position sensing of ionizing particles. Over the years a lot of improvements were made in its design and fabrication as described in many papers\(^{[20][25]}\). This opened up new possibilities in the field of high-resolution X-ray spectroscopy and imaging.
Figure 3-5 shows a schematic overview of a silicon drift detector (SDD). The bulk of the detector crystal consists of high resistivity, fully depleted, n-type Si. The silicon gets fully depleted by applying a negative bias voltage between the two sides. The side of the entrance window consists of a continuous p⁺ electrode, for improved soft X-ray detection. The other side consists of small strips of p⁺ electrodes with SiO₂ in-between, which creates local potential minima for the electrons. If an X-ray photon hits the thin radiation window and is absorbed within the volume of fully depleted Si, charge-carriers are generated. Due to the electric unbalance between anode and cathode, the electrons will drift to the small anode, positioned in the center of the device. The generated holes are absorbed by the p⁺ junctions.

The contribution of the detector to the total read-out capacitance is minimized by the small size of the collecting anode and the use of an integrated transistor in the amplifying electronics, which is needed to further process the signal. The transistor, a single sided n-JFET (junction gated field-effect transistor), is integrated in the middle of the collecting anode and is connected by a narrow metal strip. The change of the anode voltage caused by signal electrons can be measured as a variation of the transistor current. It is important that the JFET is integrated within the detector, as this provides a better resolution and a higher stability at higher count rates.

Figure 3-5: Schematic diagram of the silicon drift detector for X-ray spectroscopy.
The leakage current is the signal generated by thermal electrons, when no X-rays are present. To provide a better energy resolution and reduction of leakage current, cooling of the device is necessary. For SDD detectors, this can be conveniently done by Peltier cooling, without the need of using liquid nitrogen.

The silicon drift detector used in the MicroXRF instrument is called the SiriusSD, manufactured by the company e2v Scientific Instruments Ltd. The silicon crystal has an active thickness of 450 µm and a sensor area of 60mm². Due to the use of an internal collimator the sensor active area is reduced to 50mm².
Chapter 4: Pulse Processing

The goal of this thesis is to investigate the influence of different detector parameters on the detected XRF-spectra and on the achievable analytical characteristics, in order to know the role and optimize each detector parameter used in Chapter 6. This chapter provides a detailed description of the components of the electronic chain, present in the digital pulse processor, processing the X-ray pulses before they are properly detected.

4.1 Preamplifier

When an X-ray photon is absorbed in the active material of the detector, an electric signal is generated. This signal is lead to the preamplifier, where it is extracted without lowering the signal to noise ratio. One of the requirements is that the preamplifier is situated as close as possible to the detector.

There are two types: a reset-type and a RC-type preamplifier. In the SDD detector of the MicroXRF instrument a reset-type of preamplifier is used which will be discussed below.

![Figure 4-1: Reset-type charge sensitive preamplifier](image)

Figure 4-1 shows a schematic of a reset-type preamplifier. The X-ray pulse is collected at the detector D, the pulse is converted to an electric signal and the charge carriers are collected on the feedback capacitor $C_f$. The charge is built up and when this is too large, the output voltage can behave non-linearly. Therefore the capacitor needs to be discharged through a pulse from the input FET that opens the transistor switch S.
Figure 4-2 shows an output signal of the preamplifier. The polarity is determined by the sign of the steps. A positive step is a voltage step with a rising edge and this is defined as a positive polarity. The reset interval is the period between each reset and the restart of data acquisition. Typically this reset interval value is approximately 10 µs. By setting a value which is too high will introduce additional dead time in the detection process. When setting it too low, it can introduce artifacts in the spectrum. The preamplifier gain describes the ability to increase the power of the signal from the input to output. The preamp rise time is determined by the rising edge of a pulse created by one X-ray event.

### 4.2 Analog to Digital Converter

The purpose of an analog to digital converter is to generate a representative digital number for each analog pulse height. This number is stored in a memory and then sorted to make a histogram that constitutes the energy spectrum. If this processing can be done in a time shorter than the peaking time (explained in section 4.3.2), no additional dead time is generated.

There are two methods to capture the signal. A first is the so-called peak sensing method, where a finite time interval is inspected and the maximum value of that interval is stored. A second is when storage happens at a fixed time interval after detection. This is called the peak sampling method.
4.3 Digital Pulse Processing

When the signal is digitized, it is filtered by different algorithms to reduce the noise. This takes less processing time than analog processing, so that the resolution will be constant even at higher count rates.

4.3.1 Digital Filtering Theory

As the signal is digitized, it is no longer continuous, but instead it is a series of discrete values. A way to determine the height of the signal is to take an average of the points before the step and subtract it from the average of the points after the step, as shown in Figure 4-3.

![Figure 4-3: Digitized version of one X-ray step][21].

The differences in signal processors lie in the different selection of the region and different filter weights. One obtains a triangular filter when the gap is zero or a trapezoidal filter. When the weighting value decreases with the distance from the step, then one obtains a cusp-like filter. Points closer to the step will carry more information, so these are more important in the averaging process. A cusp-like filtering is more accurate, but has the disadvantage of limited throughput and is more expensive to realize. Therefore trapezoidal filtering is favored in commercial digital pulse processing systems.
4.3.2 Trapezoidal Filtering

In trapezoidal filtering a fixed length filter is used with a weight factor equal to unity. The calculation is made all over again each time a new signal arrives. Figure 4-4 shows the output of a filter, which has a length L and a gap G. The base width of the trapezium is 2L + G and the flat top equals G. The rise-time of the filter is also equal to L. The downside of this type of filtering is that one needs two memories to store the data, one for L and one for L+G. The memory space is restricted, so a pre-averaging of the data-stream is performed. No data is lost, but is only rearranged. By pre-averaging the data from the ADC, one gets sequential sums of D data points, where $D = 2^N$. This is called decimating by N [21].

![Figure 4-4: Trapezoidal filtering](image)

The rise time L of the trapezoidal filter is also called the peaking time and G is called the gap time. These are two parameters to adjust the output pulse. In case of data filtered by analogue electronics using a semi-Gaussian filter, the free parameter is called the shaping time. The relation between peaking and shaping-time values is as follows [23]:

$$PT = 2.2 \ ST$$  \hspace{1cm} (4-1)

where PT is peaking time and ST is shaping time, both values expressed in $\mu$s.
4.3.3 Baseline Averaging

The baseline is a reference from where the amplitude of a peak is measured. It is also subjected to the preamplifier filtering, it keeps the amplitude of the fluctuations low and diminishes its frequency. These fluctuations are referred to the electronic noise $\sigma_E$, which have a given standard deviation. The electronic noise is a function of the filter and peaking time. On top of each peak an additional noise term is present, the Fano noise $\sigma_F$, this is a function of the charge produced in the detector material (Figure 4-5). The total noise $\sigma_T$ can be written as:

$$\sigma_T = \sqrt{\sigma_E^2 + \sigma_F^2}$$  \hspace{1cm} (4-2)

Mostly the baseline value is not equal to zero and must be subtracted from the amplitude of the peak of interest. To make this error as small as possible an average of multiple baseline measurements $N_B$ is taken, so that equation 4-2 becomes:

$$\sigma_T = \sqrt{\frac{1}{N_B} \sigma_E^2 + \sigma_F^2}$$  \hspace{1cm} (4-3)

In practice a series of baseline measurements is taken in order to estimate an initial value. This value is stored and can be requested at any given time. Additional measurements are taken over time, to keep the estimated value as accurate as possible.
4.3.4 Detection and Threshold Settings

In order to measure a peak, an X-ray signal must be detected. This is done by comparing the output of the trapezoidal filtering with threshold values. There are three different filters, each with a typical threshold setting: a fast, an intermediate and a slow filter. The fast or trigger filter is used for detection only. Because it has a short flat top, it can be used for rejecting peaks that would pile-up in the spectrum and could not be detected with the slow filter. The slow or energy filter reduces the noise significantly and can be used for detection of very low energy X-rays. Because it has a slow response, most of its functions can be taken over by the intermediate filter. Only at very low count rates is an energy filter useful. The intermediate or baseline filter has an intermediate function between the fast and slow filters. It extends the detection range of the fast filter at the lower side of the energy spectrum and reduces the noise \[21\].
4.3.5 Pulse Pile-up

One can only measure the correct amplitude of a pulse if it is well separated from its previous or successive pulses. This happens if the pulse is not piled up. Therefore one examines the fast and slow filter.

Figure 4-6: A sequence of 5 pulses shown how it is seen by the preamplifier, fast filter and slow filter[21].

An example is shown in Figure 4-6: five pulses are detected and examined by the slow and fast filter. The slow pile-up, referring to pile-up in the slow filter, occurs when the rising or falling edge of one peak lies beyond an edge of another peak. In the example, pulse 1 and 2 are sufficiently separated, pulse 2 and 3 are not. The separation in the slow filter depends solely on the peaking time of the filter used. The longer the peaking time, the more pile-up will occur. The digital pulse processor tests for slow pile-up by measuring an interval PEAKINT after the arrival of a pulse. If this value is lower than the peaking time of a pulse, the pulse passes the PEAKINT-test.
The fast filter has a very short peaking time, peaks that pile-up in the slow filter can be separated in the fast filter. Pulses 1, 2 and 3 are well separated. They will pass the fast filter, but are rejected in the slow filter. Pulse 4 and 5 are occurring very close together, the output is too slow and they are seen as one single pulse in the slow filter. This pulse has neither the energy of pulse 4 or 5. This event is called a fast channel pile-up. To distinguish this kind of pile-up, one looks at the rise time of the preamplifier, which is energy independent. Therefore the base-width of the fast trapezoidal filter will also be energy independent and will never exceed the value MAXWIDTH, which is defined as two times the length of the rising edge and the length of the gap time of the fast trapezoidal filter. Whenever the width of the fast filter output pulse is greater than the value MAXWIDTH, it fails the MAXWIDTH-test, as shown by pulse 4 and 5. Fast pile-up must have occurred and this signal is rejected. From all the pulse shown in Figure 4-6, only pulse 1 will pass the pile-up test and will be processed further[21].
Chapter 5: The MicroXRF Instrument

5.1 The MicroXRF Instrument: Experimental Setup

In case of (scanning) micro-XRF spectroscopy a sample is irradiated with an X-ray beam (A), with a beam size in the micrometer range. In this way, the X-ray beam excites a microscopic volume of the sample material through the above described interactions, and the induced fluorescent radiation is detected by an energy-dispersive detector (C), which records the XRF spectrum of the induced sample response. In order to minimize scattering, and thus to reduce background and the chance to overload the detector, the preferential angle between source – sample – detector is 90 degrees [3].

The sample is mounted on a XYZ-translational stage (D). This positioning system allows the sample to be placed in the focal point of the exciting X-ray beam. Each part can be controlled via a computer system, which allows the investigation of a spot, line or area of interest in terms of (detectable) elemental distributions by various scanning strategies. For the optical observation of the sample and for the selection of the area of interest for the scanning micro-XRF analysis, a digital microscope (B) is installed.

Figure 5-1: Photograph of the MicroXRF instrument (left) and a zoom (right) showing the different parts of the set-up: X-ray source(A), microscope(B), detector(C) and sample stage with sample(D).
5.2 Characteristics

The MicroXRF is an instrument used for non-destructive elemental microanalysis. The X-ray source is a Mo-tube, manufactured by X-ray Optical Systems Inc. (XOS, Albany, USA), operated at a voltage of 40 kV. The generated X-ray beam is monochromatized and focused as it passes through the doubly curved crystal, before irradiating the sample. The generated spot size on the sample has an area of 168 µm (H) x 50 µm (V), FWHM.

The fluorescent radiation is detected by a silicon drift detector (SDD), called SiriusSD®, manufactured by e2v Scientific Instruments Ltd (UK). This detector has an active area of 50 mm² and an active thickness of 450 µm. The crystal is held under vacuum conditions to reduce effects of humidity and to reduce absorption effects. To lower thermal noise the device is cooled by a combination of Peltier cooling and active air flow.

A Beryllium window of 8 µm is used as detector window, which separates the cooled crystal from the surrounding. The beryllium window material attenuates the low energy part of the detected XRF spectra, decreasing its detectability below 2.5 keV, as shown in Figure 5-2. This graph shows the quantum efficiency of the detector crystal with this particular beryllium window thickness. The detectability is best (>90%) between 2.5 and 12 keV. At 20 keV the efficiency gets below 33% due to the high-energy transmission of X-rays through the relatively thin Si-crystal. An energy resolution up to 124 eV is measured for the Fe-Kα peak with an incoming count rate of 5000 cps.

![Figure 5-2: Plot showing the detection efficiency of a 450 µm Si crystal with an 8 µm Be window (right) and the attenuation length as a function of energy of pure Si (right). Data computed via NIST attenuation values.](image-url)
With the detector a digital pulse processor is supplied (type DX1), this digitizes the signal from the preamplifier output as explained in section 4.3. The software used to change and optimize the detector electronics is the Prospect software, version 1.0.x.

For sample positioning, a translational sample stage setup, manufactured by Physiks Instrumente (PI) GmbH (Germany) is present. The motors can move in the X-, Y- or Z-direction. Each motor has a travel range of 100 mm and an accuracy of 0.1 µm. Therefore point measurements, line and area scans can be performed using the MicroXRF instrument. Also a rotational stage is present, which enables performing XRF-tomography. During XRF-tomography a series of 2D scans are performed, each under a different angle. Afterwards a 3D image is constructed, which shows the elemental distribution in the examined sample volume.
Chapter 6: Influences of Detector Parameters

The quality of a spectrum can be influenced by a lot of different factors. How good peaks are separated, is a function of the energy resolution. The minimum detection limit gives the amount of an element in a sample that needs to be present in order to detect it. The position of a peak in an XRF spectrum is element dependent, whenever this is influenced the interpretation of a spectrum will change. The dead time will influence the analysis time. Those factors can be changed by adjusting detector parameters, such as: peaking time, minimum gap time, gain, baseline average sample and thresholds. Not all parameters will influence the XRF spectrum in such a way: the preamplifier polarity, reset interval and preamplifier rise time have an exact value and are characteristic for the preamplifier. It is important to know them in order to optimize the other detector parameters. The ideal situation would be to find a setting with the highest energy resolution, lowest minimum detection limits and low dead time, however this is not possible and a balance needs to be found.

Practically, not every combination of detector parameters could be examined. Therefore series of measurements were performed where only one parameter value was changed, to examine the spectral response in function of this detector parameter. Whenever this value was optimized, another parameter was examined in the next series of measurements. The influence on the spectral response was examined by measuring reference materials: a 4 µm, 99.85% Goodfellow iron foil and NIST standards.

An additional tool used to change and optimize the detector parameter of the MicroXRF instrument is the Prospect software. This software allows the reading out of the energy-dispersive XRF spectra response as result of the changed parameter values. Several diagnostic modes can be used to investigate the detector response, including the energy, trigger and baseline filter, the baseline history and the ADC (analog to digital converter) panel.
6.1 Preamplifier Polarity, Reset Interval and Preamplifier Rise Time

The preamplifier polarity, reset interval and preamplifier rise time are three detector parameters that don't influence the XRF spectrum directly, but they influence how the electric signal will be processed and thus important to know its value.

In the Analog to Digital Converter (ADC) panel of the ProSpect software the polarity can be checked of the MicroXRF, Figure 6-1 shows a few X-ray steps with rising edge, corresponding to a positive polarity, and a number of X-ray steps with falling edge, corresponding to a negative polarity. Since the digital filter expects an X-ray pulse with rising edge, important for further processing, a signal with a negative polarity should be revised.

![Figure 6-1: Illustration of five X-ray pulses with rising edge corresponding to a positive polarity (left) and five X-ray pulses with falling edge corresponding to a negative polarity (right).](image)

The rise time is the rising edge of the trapezoidal filter, while the gap time is the flat top length, as was explained in section 4.3.2. The preamp rise time gives information about the time required for a signal to rise from its minimum to its maximum value. To check the preamp rise time, a waveform in the ADC panel is obtained. To identify the preamp rise time, one should try to get the signal of one X-ray pulse. This is done by setting the ADC sampling period very short, around 20 ns.

When the signal corresponding to one X-ray event is isolated, the measure of the rising edge of the pulse corresponds to the 0-100% preamplifier rise time. The preamp rise time was calculated for the MicroXRF: in Figure 6-2 the value is determined by the time between the two vertical lines: 0.6 µs.
The reset interval is the period between each reset and the restart of data acquisition. This detector parameter was not known or provided in the detector data sheet, therefore a value of 10 µs was chosen, as suggested by the manual[21].

### 6.2 Peaking Time

The peaking time, or the rise time of the trapezoidal energy filter (Figure 6-3), has a great influence on the energy resolution of the detector. This was proven by performing a series of measurements with varying peaking times. A few peaking times were selected and a throughput curve was constructed, which shows the relation between the incoming and outgoing count rate. Afterwards the throughput curve of the MicroXRF was compared with the EDAX-EAGLE III, which has a Si(Li)-detector.

The relation to the energy resolution was determined by performing a series of measurements on a Goodfellow iron foil with 4 µm thickness. The free parameter was the peaking time, which was varied in the range of 0.5 to 50 µs. To determine the energy resolution, the Fe-Kα peak was fitted with a Gaussian curve and its FWHM with standard error was calculated using in-house software.

Figure 6-2: The preamp rise time of one X-ray event. The time between the two vertical lines is approximately 0.6 µs.
Figure 6-3: Output of the energy filter, with peaking time 3 µs. The response of one X-ray pulse has a trapezoidal shape.

As shown in Figure 6-4, the best energy resolution is achieved at a peaking time of 36 µs, yielding an energy resolution of 124.8 eV. When a peaking time under 2 µs is used (left from the black line), one can see that the energy resolution becomes rather poor, reaching values above 170 eV. At high peaking time values the energy resolution improves considerably, this is because a longer time is used to filter each pulse which improves the sensitivity. The drawback of this improved energy resolution is the higher dead time (DT) and therefore the longer measurement time.

The dead time is calculated by dividing the difference between incoming (ICR) and effectively detected ‘outgoing count rate’ (OCR) with the incoming count rate. It is clear that a trade-off should be made between energy resolution and dead time. For high throughput measurements, where resolution is no issue, a shorter peaking time is advised. When energy resolution has priority over measuring time, a longer peaking time needs to be used, with 36 µs providing optimum resolution. During this work, it was concluded that a peaking time of 3 µs can be used for routine measurements in order to reduce detector dead time while still achieving good energy resolution (~150 eV), while 36 µs should be selected for high energy resolution measurements (~125 eV).
Figure 6-4: The energy resolution, measured at 6.4 keV (blue), and dead time (red) versus the peaking time. The error on the energy resolution measurements lies between 0.2 and 0.5 eV. The black line marks the point where PT = 2 µs.

**Throughput curve**

Next the influence on the count rate was examined, therefore a throughput curve was determined for several peaking times. For this experiment the Goodfellow iron foil was measured and the current of the tube was gradually increased to increase the count rate. This procedure was repeated for each selected peaking time. When the outgoing count rate is plotted as a function of the incoming count rate, one obtains a linear relationship in case of the short peaking times, as seen in Figure 6-5. The range of the linear relation is peaking time dependent. With low PT, the linear relation is valid over the whole range of the plot. Whenever the PT increases, the range of the linear relation becomes shorter and shorter and a horizontal slope is obtained at higher count rates. When the ICR is increased, the OCR (i.e. the effectively detected count rate) will stay the same, only its dead time will increase as shown in Figure 6-6. The increase in dead time is not desirable, each measurement will take longer and longer, but the OCR won’t increase. When decreasing the ICR, the same OCR can be obtained and the measurement will take less time. At short peaking times, e.g. the 3 µs chosen for automated routine measurements, there is no problem. The linear relation between DT and OCR applies over a wider range, only at very high count rate the vertical slope will appear.
Figure 6-5: Outgoing count rate versus incoming count rate. Measurements were performed on an iron foil, setting the tube at 40 kV and varying current; 100 s LT.

Figure 6-6: Dead time versus the outgoing count rate. Measurements were performed on an iron foil, setting the tube at 40 kV and varying current; 100 s LT.
Figure 6-7: The energy resolution versus the incoming count rate. Measurements were performed on an iron foil, setting the tube at 40 kV and varying current; 100 s LT. The error on the measurements lies between 0.2 and 0.5 eV.

Figure 6-8: The Fe-Kα peak area versus the incoming count rate. Measurements were performed on an iron foil, setting the tube at 40 kV and varying current, 100 s LT. The error on the Fe peak area lies between 900 and 2500 counts.
Figure 6-9: Zoom of Figure 6-8 at 0.5 mA, showing the variation of the Fe-Kα peak area (left) and the ICR (right) as a function of the PT. Measurements were performed on an iron foil, setting the tube at 40 kV and 0.5 mA (± 5400 cps), 100 s LT.

Also the variance in the energy resolution and peak area of the Fe-Kα was investigated. The Fe-Kα peak was determined using specialized software; AXIL\textsuperscript{[28]} and the standard error was determined by taking the square root of the peak area.

One can see in Figure 6-7 and Figure 6-8 that the count rate and therefore the X-ray tube current have no visible influence on the resolution and the peak area of the Fe-Kα peak. One can see in Figure 6-9 that the only variation in the peak area comes from the instability of the incoming count rate.

**MicroXRF versus EDAX EAGLE-III**

In order to compare how well the MicroXRF performs in terms of energy resolution and throughput, it is compared with the EDAX EAGLE-III. This instrument uses a Rh-tube as X-ray source and typically operates at a voltage of 40 kV. The X-ray beam is focused by the use of a polycapillary optic. There is a possibility to vary the spot size by defocussing the polycapillary using the so-called VariSpot option. The sample is mounted on a stage, which can move in the X-, Y- and Z-direction. The sample chamber in this case is completely sealed and has the possibility to operate in a vacuum environment, making the detection of low energy X-ray lines easier. The Si(Li)-crystal in the detector has an active surface of 80 mm\(^2\) and is sealed by a beryllium window. The detector is cooled by liquid nitrogen.
The same experimental procedure as described in section 6.1 was used to get the throughput curve: the tube current was gradually increased to obtain an increased count rate.

The EDAX EAGLE-III has a shaping time of 17 µs, which corresponds to a peaking time of 37.5 µs. Figure 6-10 shows the throughput curve of both instruments. The MicroXRF is operated at 36 µs, which is the setting for optimal resolution. The setting of the Eagle is more a trade-off between throughput and resolution. It is a standard setting that is never changed. For routine measurements the guideline with this instrument is to optimize the current in such a way that the detector dead time never exceeds 30 % DT which correspond roughly to 5000 cps. The MicroXRF has a much shorter peaking time (3 µs) for routine measurements, which results in a higher throughput with lower dead time. The energy resolution at the Fe-Kα peak for routine measurements with the MicroXRF is 150 eV, while with the Eagle it is 164 eV.

![Figure 6-10: Outgoing count rate versus incoming count rate. The EDAX EAGLE-III was operated with a shaping time 17 µs, the MicroXRF with peaking times 3 and 36 µs.](image-url)
6.3 Minimum Gap Time

The minimum gap is the second most important parameter to improve the energy resolution, also the influence on dead time was investigated. Normally the minimum gap time should be greater than the preamplifier rise time to fully detect the pulse. The preamplifier rise time is 0.6 µs for almost every peaking time as shown in section 6.1. Therefore the minimum gap time should be set at a higher value than 0.6 µs. To be sure this statement is valid, the minimum gap time was set to a value between 0 and 1.2 µs and three peaking times were selected: a low value (0.8 µs), the value for routine measurements (3 µs) and a high value (20 µs).

At a peaking time of 3 µs, one can see that the dead time is increasing whenever the minimum gap time increases. The energy resolution increases to a maximum and then decreases significantly. The optimum minimum gap time is approximately 0.6 µs, which is greater than the preamp rise time.

![Graph showing variation in energy resolution and dead time](image)

Figure 6-11: The variation in energy resolution and dead time (PT = 3 µs). Measurements were performed on an iron foil, setting the tube at 40 kV and 0.5 mA (± 5400 cps); 100 s LT.
Figure 6-12: The variation in energy resolution and dead time (PT = 20 µs). Measurements were performed on an iron foil, setting the tube at 40 kV and 0.5 mA (± 5400 cps); 100 s LT.

At a peaking time of 20 µs, the dead time stays constant and the energy resolution only varies with 1.5 eV. As a result of this, one can conclude that the minimum gap time is not a limiting variable at higher peaking times.

Figure 6-13: The variation in energy resolution and dead time (PT = 0.8 µs). Measurements were performed on an iron foil, setting the tube at 40 kV and 0.5 mA (± 5400 cps); 100 s LT.

At a peaking time of 0.8 µs, the dead time increases at the same rate as in case of a peaking time of 3 µs. The energy resolution is also going to a maximum, but its decrease is not that significant in comparison with the peaking time set at 3 µs. By looking only at this, the optimum value of the minimum gap time should be 0 µs. When looking at the spectrum (Figure 6-14), we see that below a value of 0.6 µs the gain changes significantly. Above 0.6
µs, the gain stays constant and one can conclude that also here the optimal value is higher than the preamp rise time.

Figure 6-14: XRF spectrum showing the iron foil using two different minimum gap times. Measurements were performed on an iron foil, setting the tube at 40 kV and 0.5 mA (± 5400 cps); 100 s LT.

To conclude, it can be stated that the best setting of the minimum gap time is higher than the preamp rise time. With the peaking time for routine measurements (3 µs) this was clearly visible, with the lower peaking time problems with the gain arose when the minimum gap time was lower than the preamp rise time and with higher peaking time no change was seen.

6.4 Baseline Average Sample

Another parameter that influences the energy resolution is the baseline average sample (BAS), it refers to the sampling number used to get an initial value of the baseline as explained in section 4.3.3. The change in BAS was investigated on an iron foil with respect to its effects on energy resolution and dead time. Three peaking times were selected; a low value (0.8 µs), the value for routine measurements (3µs) and a high value (20 µs), and the BAS was changed during each measurement.
In terms of energy resolution we can see a dramatic decrease for a peaking time of 3 µs when more samples are acquired, for peaking times of 1.5 and 20 µs, the decrease is less significant. Figure 6-15 shows the comparison in energy resolution at the iron peak for a low and moderate baseline average sample. When the BAS is set to 100, the baseline value is accurate enough to get the best resolution (Figure 6-16 left). Increasing the BAS will not change this baseline value and the resolution will not improve. The dead time does not change when more samples are acquired (Figure 6-16 right).

Figure 6-15: Comparison in energy resolution with low (2) and moderate (2048) baseline average sample. Measurements were performed on an iron foil, setting the tube at 40 kV and 0.5 mA (± 5400 cps); 100 s LT.

Figure 6-16: Plot showing the energy resolution (left) and the dead time (right) in function of the baseline average sample at peaking time 1.5, 3 and 20 µs. Measurements were performed on an iron foil, setting the tube at 40 kV and 0.5 mA (± 5400 cps); 100 s LT.
That a low BAS must be avoided is not only seen in the energy resolution. When looking at the baseline waveform, still a lot of electronic noise is present (Figure 6-17 A). Increasing the BAS, did improve energy resolution, but at a very high number of sampling no frequency fluctuations was seen (Figure 6-17 B). The preference was given to a moderate BAS. (Figure 6-17 C).

Figure 6-17: The baseline waveform with the BAS set too low; 2 (A), BAS set too high; 65536 (B) and BAS set correctly; 2048 (C)
6.5 Thresholds

The thresholds have a wide variety of influences on the XRF spectrum. It is responsible for the low energy cut-off, it can induce reduced Compton and Rayleigh peaks and in the worst case it induces a zero energy noise peak. There are three different threshold values: the trigger-, baseline- and energy threshold, which must be optimized to detect a pulse as optimal as possible. These three threshold are closely connected. The value of the trigger threshold must be optimized first, before changing the other thresholds. Every threshold needs to be readjusted whenever the gain is changed, more information about the gain is given in section 6.6. All measurements were performed on an iron foil and were measured with a tube setting of moderate power (40 kV, 0.5 mA).

6.5.1 Trigger Threshold

The trigger or fast threshold is used for pile-up inspection, it sets a lower limit for the fast filter, explained in section 4.3.5. It is important to set this value not too low, since it will introduce a zero energy noise peak. This kind of peak is introduced when the noise is not properly filtered and it can be observed in the XRF spectrum. To investigate the proper value, one sets the baseline threshold to zero and change the trigger threshold accordingly. The peaking time is set to 3 µs and the preamp gain to 15 mV/keV. The induced change in dead time and energy resolution is investigated. Also, the XRF spectrum is examined in order to eliminate the zero energy noise peak.

![XRF spectrum of the Fe foil, trigger threshold = 50 eV (left) and trigger threshold = 800 eV (right). Tube conditions were: 40 kV and 0.5 mA (± 5200 cps); 100 s LT.](image)
Table 1 shows the incoming and outgoing count rate, dead time and energy resolution values with their standard deviation. The dead time is calculated by dividing the difference between incoming and outgoing count rate by the incoming count rate. The energy resolution is obtained by fitting a Gaussian curve to the Fe-Kα peak at 6.4 keV.

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<th>Trigger Threshold (eV)</th>
<th>ICR (cps)</th>
<th>OCR (cps)</th>
<th>DT (%)</th>
<th>Resolution (eV) @ 6.4 keV</th>
<th>Std. deviation</th>
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</tr>
<tr>
<td>500</td>
<td>5559</td>
<td>5260</td>
<td>5.38</td>
<td>150.1</td>
<td>0.2</td>
</tr>
<tr>
<td>600</td>
<td>5541</td>
<td>5252</td>
<td>5.22</td>
<td>150.2</td>
<td>0.2</td>
</tr>
<tr>
<td>700</td>
<td>5458</td>
<td>5186</td>
<td>4.99</td>
<td>149.8</td>
<td>0.2</td>
</tr>
<tr>
<td>800</td>
<td>788</td>
<td>757</td>
<td>3.97</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>900</td>
<td>130</td>
<td>107</td>
<td>17.17</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>1000</td>
<td>129</td>
<td>107</td>
<td>17.32</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

Table 1: Influence of dead time and energy resolution as function of trigger threshold, when the baseline threshold is set to zero. Measurements were performed on an iron foil with tube conditions 40 kV and 0.5 mA (± 5200 cps; 100 s LT).

At a threshold value of 0 eV, no spectrum is detected: the trigger is shut down and nothing passes through. At threshold values of 50 and 100 eV, the incoming count rate is too high: this is because a zero energy noise peak is introduced and noise is seen as an X-ray pulse. This causes a significant increase in the detected count rate and the dead time. In Figure 6-18 (left) the pile-up and scatter peaks are distorted: their energy was incorrectly filtered. Between threshold values of 150 and 800 eV, the dead time and energy resolution remains constant. The limiting factor here is the low energy cut-off, as shown in Figure 6-19, and the reduced Compton and Rayleigh peaks. Above 800 eV, the Fe-Kα peak is cut-off and the energy resolution cannot be determined, as shown in Figure 6-18 (right).
Figure 6-19: XRF spectrum of the iron foil showing the low energy cut-off at different trigger thresholds. Tube conditions were: 40 kV and 0.5 mA (± 5200 cps); 100 s LT.

Figure 6-20: XRF spectrum of the iron foil showing the reduced scatter peaks with gain 3.5 mV/keV. Tube conditions were: 40 kV and 0.5 mA (± 5200 cps); 100 s LT. The baseline threshold was set at 0 eV.
With the gain of 15 mV/keV the optimal value is determined to be above 150 eV: it is important to set this value as low as possible, paying attention that the Compton and Rayleigh peaks are fully visible. When the gain is changed, the trigger threshold must be adapted accordingly. With a gain of 3.5 mV/keV, the trigger is shut down below 100 eV, and nothing is detectable in the XRF spectrum. Between 100 and 200 eV, a zero energy noise peak can be observed and no Compton and Rayleigh peaks appear. Between 200 and 400 eV, reduced Compton and Rayleigh peaks appear (Figure 6-20). In this case (gain of 3.5 mV/keV), the optimal value is found to be above 700 eV.

Whenever the peaking time is changed, the trigger threshold does not need to be optimized, since the peaking time is connected to the energy filter and not to the fast filter.

### 6.5.2 Baseline Threshold

The baseline or intermediate threshold is used for the detection of low energy X-rays and the acquisition of the baseline. Whenever an optimal value of the trigger threshold is determined, the baseline threshold must be optimized. The peaking time is set to 3 µs and the preamp gain to 15 mV/keV. The possible change in dead time and energy resolution is investigated as a function of baseline threshold. At first the XRF spectrum is examined, because the zero energy noise peak will reappear and must be eliminated. One needs to emphasize that a zero energy noise peak should be avoided in all cases. With this kind of peak, the detector can behave inconsistently e.g. with respect to dead time, which affects the measurements.

The ICR and OCR, dead time and energy resolution with its standard deviation are summarized in Table 2. When the baseline value increases to 50 eV, the zero energy noise peak reappears and the incoming count rate becomes too high due to improper noise filtering (Figure 6-21). The energy resolution and dead time are no limiting factors in this case and are constant over the whole range. The optimal baseline threshold value is determined to be above 100 eV, the exact value is dependent on the low energy cut-off (Figure 6-22). Therefore a sample containing an element with a low atomic number, e.g. aluminum, was measured while examining the XRF spectrum: the value of the baseline threshold was set in such a way that the Al peak was not cut off.
<table>
<thead>
<tr>
<th>Baseline Threshold (eV)</th>
<th>ICR (cps)</th>
<th>OCR (cps)</th>
<th>DT (%)</th>
<th>Resolution (eV) @ 6.4 keV</th>
<th>Std. deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>6705</td>
<td>6450</td>
<td>3.80</td>
<td>150.6</td>
<td>0.3</td>
</tr>
<tr>
<td>100</td>
<td>5526</td>
<td>5250</td>
<td>5.00</td>
<td>150.3</td>
<td>0.3</td>
</tr>
<tr>
<td>150</td>
<td>5545</td>
<td>5265</td>
<td>5.05</td>
<td>150.9</td>
<td>0.2</td>
</tr>
<tr>
<td>200</td>
<td>5540</td>
<td>5264</td>
<td>4.98</td>
<td>150.8</td>
<td>0.2</td>
</tr>
<tr>
<td>250</td>
<td>5529</td>
<td>5259</td>
<td>4.88</td>
<td>150.1</td>
<td>0.2</td>
</tr>
<tr>
<td>300</td>
<td>5534</td>
<td>5260</td>
<td>4.94</td>
<td>151.5</td>
<td>0.2</td>
</tr>
<tr>
<td>350</td>
<td>5511</td>
<td>5240</td>
<td>4.92</td>
<td>151</td>
<td>0.3</td>
</tr>
<tr>
<td>400</td>
<td>5518</td>
<td>5246</td>
<td>4.93</td>
<td>150.8</td>
<td>0.2</td>
</tr>
<tr>
<td>500</td>
<td>5520</td>
<td>5251</td>
<td>4.87</td>
<td>150.9</td>
<td>0.2</td>
</tr>
<tr>
<td>600</td>
<td>5492</td>
<td>5224</td>
<td>4.88</td>
<td>151</td>
<td>0.2</td>
</tr>
<tr>
<td>700</td>
<td>5498</td>
<td>5227</td>
<td>4.92</td>
<td>151</td>
<td>0.2</td>
</tr>
<tr>
<td>800</td>
<td>5501</td>
<td>5238</td>
<td>4.79</td>
<td>150.4</td>
<td>0.2</td>
</tr>
<tr>
<td>900</td>
<td>5496</td>
<td>5232</td>
<td>4.82</td>
<td>151.3</td>
<td>0.2</td>
</tr>
<tr>
<td>1000</td>
<td>5490</td>
<td>5234</td>
<td>4.67</td>
<td>151.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 2: Influence of dead time and energy resolution as function of the baseline threshold, when the trigger threshold is set to an optimum, here 300 eV.

Figure 6-21: XRF spectrum of the iron foil showing the reappearing of the zero energy noise peak with baseline threshold = 50 eV. Tube conditions were: 40 kV and 0.5 mA (± 5200 cps); 100s LT.
Figure 6-22: XRF spectrum of the iron foil showing the low energy cut-off at different baseline thresholds. Tube conditions were: 40 kV and 0.5 mA (± 5200 cps); 100s LT. The trigger threshold was set at 300 eV.

Whenever the gain is changed, the baseline threshold value must be optimized again. For example, when the gain is set to 3.5 mV/keV, the optimal value of the baseline threshold is set above 600 eV. Below this value the zero energy noise peak is reappearing. Unlike the trigger threshold, the baseline threshold value should be optimized whenever the peaking time is changed.

6.5.3 Energy Threshold

The energy or slow threshold is used for determining the pulse height of the voltage steps. Because in most cases the energy threshold introduced an error in the counting statistics, it is recommended to set this value at zero.\textsuperscript{21}
6.6 Gain

The gain plays an important role in the position of the peak in an XRF spectrum. Two important gains, that are investigated closer, are the preamp gain and the MCA bin width. Their relation with each other and with the number of bins are described. A comparison between two preamp gains was made also, their performance in energy resolution, dead time and minimum detection limit was investigated.

The first gain that is discussed is the preamplifier gain. The preamplifier is the interface between detector and the pulse processor, as described in section 4.1. The extracted signal needs to be amplified without significantly degrading the signal to noise ratio, this level of amplification is determined by the preamp gain. The Prospect software provides a function to calibrate the gain. An XRF spectrum is taken and a region of interest is chosen. In Figure 6-23 an iron foil is measured and the region of interest (between the two vertical lines) is the Fe-Kα peak. The exact energy (6.404 keV) is filled in and the software can calibrate the gain. This is an iterative process, whenever the gain stays constant, this value can be chosen as preamp gain. The preamp gain of the MicroXRF has a value of 3.5 mV/keV, as given in the specifications. Calibrating with the ProSpect software gives roughly the same value.

![Image](image.png)

Figure 6-23: Illustration of an XRF spectrum, taken with the Prospect software, used to calibrate the preamp gain using the Fe-Kα peak.
The MCA bin width is also a gain, expressed in eV/channel or eV/bin. Other synonyms are system gain or conversion gain. This setting determines the size of each MCA bin. Figure 6-24 shows an XRF spectrum with 2 different bin width. The energy on the x-axis is calibrated with a bin width of 10 eV/bin (blue line) and by changing the bin width to a lower value (red line), the peak position changes and therefore the energy axis must be recalibrated.

The MCA bin width is inversely proportional with the preamplifier gain. Whenever the preamp gain is set to a higher value, the MCA bin width must set to a lower value. For example in case of the MicroXRF instrument, if the preamp gain is increased from 3.5 to 15 mV/keV, the MCA bin width must be reduced from 9.72 to 2.29 eV/bin.

![Figure 6-24](image)

Figure 6-24: Illustration of the influence of the MCA bin width. Measurements were performed on an iron foil, setting the tube at 40 kV and 0.5 mA (± 5400 cps); 100 s LT.

The number of bins can also be adjusted, this sets the granularity of the spectrum. The more bins are used, the smoother the spectrum looks as shown in Figure 6-25. This value in combination with the MCA bin width should not exceed the value of the dynamic range. X-rays with an energy exceeding the value of the dynamic range cannot be processed properly. The value of the dynamic range is determined by the largest X-ray energy present. In the MicroXRF, the MCA bin width is set to 9.72 eV/bin and the number of bins to 2048. Multiplying these values gives 19906 eV, which is smaller than 19983 eV, defining the
dynamic range value of the MicroXRF instrument. This dynamic range value needs to be higher than the energy of the Mo-K$_\beta$, originating from the Mo-tube.

![Graph showing intensity counts over MCA channel number]

Figure 6-25: Illustration of the influence of the number of bins. Measurements were performed on an iron foil, setting the tube at 40 kV and 0.5 mA (± 5400 cps); 100 s LT.

**Comparing the performance of two preamp gains**

An evaluation of the XRF spectrum was performed between two preamp gains; 3.5 mV/keV, the manufacturer’s recommended setting, and 15 mV/keV. Their performance in dead time and energy resolution was examined by measuring an iron foil, the MDL by measuring SRMs. Table 3 shows the result of the comparison with the iron foil, the higher preamp gain has a lower dead time and better energy resolution.

<table>
<thead>
<tr>
<th>Preamp Gain (mV/keV)</th>
<th>3.544</th>
<th>15.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dead Time (%)</td>
<td>5.5</td>
<td>4.4</td>
</tr>
<tr>
<td>Energy Resolution (eV)</td>
<td>148.1 ± 0.1</td>
<td>147.3 ± 0.1</td>
</tr>
</tbody>
</table>

Table 3: Table showing the dead time and energy resolution at different preamplifier gain values. Measurements were performed on an iron foil, setting the tube at 40 kV and 0.5 mA (± 5400 cps), 100 s LT.
The minimum detection limits (MDL) values were determined from a stainless steel sample, NIST SRM 1155, corresponding to a measurement of 1000 s LT. The tube voltage was set to 40 kV and to a current of 0.4 mA. The most important parameters are listed in Table 4. As explained above, whenever the gain is changed, the MCA bin width, trigger threshold and baseline threshold needs to be readjusted. One can conclude that the minimum detection limit values are slightly lower when measuring with the preamp gain of 15 mV/keV (Figure 6-26).

<table>
<thead>
<tr>
<th>Preamp Gain (mV/keV)</th>
<th>3.544</th>
<th>15.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peaking Time (µs)</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>MCA Bin Width (eV/bin)</td>
<td>9.72</td>
<td>2.29</td>
</tr>
<tr>
<td>Trigger Threshold (eV)</td>
<td>800</td>
<td>300</td>
</tr>
<tr>
<td>Baseline Threshold (eV)</td>
<td>700</td>
<td>200</td>
</tr>
<tr>
<td>Bin Samples</td>
<td>2048</td>
<td>2048</td>
</tr>
</tbody>
</table>

Table 4: Parameter settings when comparing 2 different preamp gains.

Figure 6-26: The difference in MDL values for two different preamp gains for the NIST SRM 1155. The error bars are taken at the 95% confidence interval. Tube conditions were: 40 kV and 0.4 mA (± 8000 cps); 1000 s LT.
The same was done for a biological matrix, the bovine liver, NIST SRM 1577c. The sample was irradiated for 1000 s LT with a tube set at 40 kV and 0.7 mA. The same parameters were used as the ones indicated in Table 4.

![Figure 6-27: The difference in MDL values for two different preamp gains for the NIST SRM 1577c. The error bars are taken at the 95% confidence interval. Tube conditions were: 40 kV and 0.7 mA (± 300 cps); 1000 s LT.](image)

Also slightly better values were obtained for the preamplifier gain value of 15.0 mV/keV with respect to minimum detection limits. By looking at these parameters, the preference was given to the higher gain.

Unfortunately, some other problems were discovered, when performing more measurements. When following an experiment in real time, sometimes a spike in dead time was observed, so that experiments using a given live time, required excessive measuring times. Due to the random nature of these spikes, a mapping consisting of a series of point measurements of 1 s LT were performed in order to observe this phenomenon. The first measurements were performed at a low count rate and the intensity was increased gradually with each experiment in order to determine the upper level where the anomalies did not occur anymore. The NIST SRM 613 was measured 1000 times with 1 s LT. The tube
parameters were set to 40 kV and 0.4 mA, which gave a count rate of 1100 cps. With this count rate the anomaly occurs with 15 mV/keV and does not with 3.5 mV/keV. As shown in Figure 6-28, the incoming and outgoing count rates have a linear relationship. In case of the preamplifier gain value of 15 mV/keV, we can see some outliers, while with the preamplifier value of 3.5 mV/keV these do not occur. The same conclusions can be drawn from Figure 6-29, where the dead time is shown instead of the OCR.

It is therefore better to use the manufacturer’s recommended setting for the preamplifier gain. Now, the upper level of the count rate where the outliers do not occur must be determined for this preamp gain. The same experiment was performed using the glass standard reference material NIST SRM 613, which was measured 1000 times for 1 second. The tube parameters were set to 40 kV and the current was increased gradually to obtain an increasing count rate. Above 800 cps, outliers were no longer observed.

Figure 6-28: The OCR versus ICR for preamp gain 3.5 (left) and 15 mV/keV (right). Tube conditions were: 40 kV and 0.4 mA (± 1100 cps); 1000 x 1 s LT.

Figure 6-29: The dead time versus number of points acquired for preamp gain 3.5 (left) and 15 mV/keV (right). Tube conditions were: 40 kV and 0.4 mA (± 800 cps); 1000 x 1 s LT.
For further measurements it is important to take into account this behavior. One should only measure real time whenever a sample has low count rate, lower than 800 cps, and a precise quantitative analysis is necessary.
Chapter 7: Summary and Conclusions

The aim of this thesis was to find an ideal combination of detector parameters, that could be used for automated routine measurements, for a newly developed laboratory MicroXRF instrument. The unique combination of a large area silicon drift detector and a monochromatic X-ray source, based on the combination doubly curved crystal optics and a Mo microfocus-tube. This combination makes the MicroXRF instrument a powerful tool for non-destructive elemental analysis down to trace concentration levels. The good performance at high count rate and its excellent signal to background ratio allows the detection of transition metals down to sub-ppm levels, and an easier and more accurate quantification. Since the different detector parameters have an enormous influence on the analytical performance of this instrument, these parameters were carefully optimized during these studies. Important analytical parameters studied were energy resolution, throughput, dead time, position of the peak, minimum detection limits, the low energy cut-off and the correct display of the scatter peaks. Three detector parameters: the polarity, reset interval and preamp rise time, have a fixed value and their spectral response was not examined.

Initially the peaking time was optimized, this parameter had the greatest influence on the energy resolution: higher values of this parameter result in a better energy resolution. This improved resolution had the drawback of a higher dead time and thus longer analysis time. Therefore a peaking time of 3 µs was found to be a good compromise for automated routine measurements: much lower dead times were obtained, with still a good resolution (150 eV). Looking at the throughput curve, the linear relation between the incoming and outgoing count rate was still valid at 9000 cps for this peaking time. For measurements aiming at high energy resolution, a peaking time of 36 µs can be recommended. Using this peaking time value, an energy resolution of 124 eV was achieved, but the linear relation between ICR and OCR is only valid at low count rates.

Other detector parameters that influence the energy resolution are the minimum gap time and baseline average sample, their values were optimized to get the best energy resolution possible.
Optimal values for the thresholds: trigger-, baseline- and energy threshold, were determined. At first the baseline threshold was shut down (setting the value at zero) in order to optimize the trigger threshold. Afterwards the baseline threshold was determined with the optimized trigger threshold value. It was important that the zero energy noise peak was avoided, this kind of peak makes the detector behave inconsistent in terms of dead time and thus analysis time. The scatter peaks must be fully visible and the low energy cut-off needs to be determined with a sample containing an element with low atomic number (e.g. Al). For the energy threshold, there was opted to set this value at zero, because it could introduce a statistical error in the counting statistics. Whenever the gain or peaking time was changed, the trigger and baseline threshold values need to be re-evaluated.

Two gains play an important role in the peak position: the preamp gain and the MCA bin width. These two values are inverse proportional and needs to be optimized together.

A comparison was made between the preamp gain of 3.5 mV/keV, the manufacturers recommended setting, and 15 mV/keV. The higher gain had better results in terms of dead time, energy resolution and minimum detection limit. Unfortunately at low count rates, the ICR was sometimes calculated incorrectly. In case of 3.5 mV/keV setting, this occurred less frequently and therefore this preamplifier gain setting is advised for future use.

<table>
<thead>
<tr>
<th>Detector parameter</th>
<th>Influence on</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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<td>Polarity</td>
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<td>+</td>
</tr>
<tr>
<td>Reset interval (µs)</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Preamp rise time (µs)</td>
<td></td>
<td>0.6</td>
</tr>
<tr>
<td>Peaking time (µs)</td>
<td>PT</td>
<td>3</td>
</tr>
<tr>
<td>Minimum gap time (µs)</td>
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</tr>
<tr>
<td>Baseline average sample</td>
<td>BAS</td>
<td>2048</td>
</tr>
<tr>
<td>Preamp gain (mV/keV)</td>
<td></td>
<td>3.5</td>
</tr>
<tr>
<td>MCA bin width (eV/bin)</td>
<td></td>
<td>9.72</td>
</tr>
<tr>
<td>Number of bins</td>
<td></td>
<td>2048</td>
</tr>
<tr>
<td>Dynamic range (keV)</td>
<td></td>
<td>19,983</td>
</tr>
<tr>
<td>Trigger threshold (eV)</td>
<td>TT</td>
<td>800</td>
</tr>
<tr>
<td>Baseline threshold (eV)</td>
<td>BT</td>
<td>700</td>
</tr>
<tr>
<td>Energy threshold (eV)</td>
<td>ET</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5: An overview of the selected parameters for an automated routine measurement.
To conclude, an overview of the detector parameters selected for an automated routine measurement, with its influence on the spectral response, is given in Table 5. When measuring the iron foil, this combination of settings gave an energy resolution of approximately 150 eV for the Fe-K\(\alpha\) peak and a dead time of 5% with an average count rate of 5000 cps.
Bibliography


[23] Amptek, Application Note: AN-SDD-001 Rev B0.


De MicroXRF is een micro X-straal fluorescentie spectrometer die recent in gebruik is genomen door de XMI onderzoeksgroep van de Vakgroep Analytische Chemie van de Gentse Universiteit (België). De combinatie van een silicium drift detector (SDD) met een monochromatisch X-straal bron maakt dit een uniek toestel. Om het potentieel van dit instrument ten volle te benutten werd de invloed van de verschillende parameters van het detectie systeem (b.v. peaking time, minimum gap time, gain en thresholds) bestudeerd. Hiervoor werd de kwaliteit van de XRF spectrale respons in detail onderzocht in termen van energie resolutie, dode tijd, telsnelheid, piek positie en lage energie afsnijding. Uiteindelijk werden de ideale waarden voor deze parameters bekomen die nuttig kunnen zijn voor geautomatiseerde routine metingen. 

**Kernwoorden:** µ-XRF, SDD, monochromatisch, detector elektronica parameters

**Inleiding**

X-straal fluorescentie (XRF) spectroscopie is een niet-destructieve, gevoelige techniek en dus een geschikte methode voor het analyseren van o.a. waardevolle objecten, biologische en geologische monsters. In het labo van de UGent XMI onderzoeksgroep werd vrij recent de zogenaamde MicroXRF spectrometer in gebruik genomen voor zulk onderzoek. Dit toestel is uniek omdat het gebruik maakt van een energie dispersieve detector in combinatie met een monochromatische bron, met als voordeel van (1) een veel hogere signaal tot achtergrondsverhouding en (2) de makkelijker kwantificatie door eliminatie van onzekerheden geassocieerd met de polychromatische energie distributie van de inkomende straal\(^1\)\(^2\). De gebruikte energie dispersieve detector is een silicium drift detector (SDD), gekend voor de goede energie resolutie bij hoge telsnelheden en de lage elektronische ruis\(^20\). De X-stralen bron is gebaseerd op een molybdeen-buis die is gekoppeld aan *doubly curved crystals* (DCC) optica, die de straling monochromatiseert en focussert\(^16\). Een positioneringssysteem laat toe om XRF beeldvorming uit te voeren door het bevestigde monster op systematische wijze doorheen de bekomen microscopische X-stralen bundel te bewegen. Het doel van dit werk is om via de studie van de invloed van de detector parameters op de kwaliteit van de opgenomen XRF spectra, optimale waarden voor deze parameters te bekomen die nuttig kunnen zijn voor zulke geautomatiseerde en routinematig uitgevoerde metingen.
Experimenteel

Figuur 1 toont de verschillende onderdelen van de gebruikte MicroXRF spectrometer: (A) de bron, (B) de optische microscoop, (C) de detector, en (D) het monster positioneringssysteem. Alle onderdelen kunnen bestuurd worden via een computer systeem wat toelaat om naast eenvoudige puntmetingen ook lijn scans en XRF beeldvorming uit te voeren van het monster. De bron, welke geleverd werd door de firma X-ray Optical Systems Inc. (XOS, Albany, VS), bestaat uit een combinatie van een 50W molybdeen X-straal buis en bijpassende DCC optica waardoor een monochromatisch en gefocusseerde X-stralen bundel wordt bekomen met grootte 120 µm × 50 µm in het focaal punt op afstand 32 mm. Het te onderzoeken monster wordt bevestigd op een positioneringssysteem bestaande uit een XYZ motorsysteem (Physiks Instrumente (PI) GmbH, Germany), wat toelaat om het monster in het focaal punt te plaatsen, gebruikmakend van de digitale microscoop (Dino-Lite, Taiwan). De uitgezonden fluorescente straling, karakteristiek voor het bestraalde materiaal, wordt gedetecteerd door een energie dispersieve detector van het SDD type (siliciumin drift detector) (5), gefabriceerd door de voormalige firma e2v Scientific Instruments Ltd (VK). Deze detector heeft een 450 µm dik siliciumin kristal met een bruikbaar oppervlak van 50 mm²; een 8 µm dik beryllium venster zorgt voor het behoud van de vacuum condities, ook is een Peltier koeling voorzien. De bijgeleverde digitale puls processor is van het type DX1. De software gebruikt om de detector parameters te optimaliseren is de Prospect software, versie 1.0.x, die toelaat de XRF spectrale respons te bestuderen als resultaat van de geselecteerde parameter waarden.

Figuur 1: MicroXRF (links) en vergroting van de verschillende delen (rechts): X-stralen bron (A), microscoop (B), siliciumin drift detector (C), monsterhouder (D).

Voor de studie van de invloed van deze parameters werden metingen uitgevoerd op referentiematerialen (o.a. 4 µm dik 99,85 % zuiver Goodfellow ijzerfolie en NIST standaarden). Enkel de resultaten die bekomen werden met de ijzerfolie worden getoond en bediscussieerd in dit werk. Als instelling voor de bron werd geopteerd voor een gematigd vermogen van 40 kV en 0,5 mA. Omdat niet elke combinatie van alle detector parameters praktisch kon worden onderzocht, werden reeksen van metingen uitgevoerd waarbij slechts één parameter waarde werd veranderd, om zo het verloop van de spectrale respons te onderzoeken in functie van die parameter. Bijvoorbeeld na de bepaling van de preferentiële waarde voor de peaking time, werden andere parameters met deze waarde verder onderzocht en bediscussieerd in een volgende reeks metingen. Detector elektronica parameter waarden van de peaking time, minimum gap time en baseline average sample werden onderzocht in functie van de energieresolutie. De waarden van de preamp gain, MCA bin width en kanaalnummer werden onderzocht in functie van de piek positie en de waarden van de thresholds op basis van zijn
invloed op de lage energie afsnijding en de verstrooiingspieken in het XRF spectrum. Andere detector parameters hadden een vaste waarde: de polariteit was positief, de reset interval had een waarde van 10 µs en een waarde van 0,6 µs voor de preamp rise time werd vastgesteld a.d.h.v. de Prospect software.

Energie resolutie, piek positie en dode tijd zijn analytische kenmerken van het XRF spectrum die de kwaliteit van de XRF spectrale respons bepalen. Voor de evaluatie van de energie resolutie werd de maximale breedte op halve hoogte (FWHM) van de gefitte Gaussiaanse curve doorheen de Fe-Kα fluorescente piek berekend samen met de fout op deze waarde met eigen software. De detector dode tijd wordt berekend door het verschil van inkomende en de effectief gedetecteerde uitgaande telsnelheid (OCR) te delen door de inkomende telsnelheid (ICR).

**Resultaten en Discussie**

Energie resolutie in functie van *peaking time, minimum gap time en baseline average sample*

De belangrijkste parameter die de energie resolutie beïnvloedt, is de *peaking time* (PT). Deze parameter wordt bepaald door de hellende kant van de trapeziumvormige energie filter\[21\]. In Figuur 2 wordt de energie resolutie en dode tijd uitgezet in functie van de PT.

Figuur 2: De energie resolutie (blauw) en dode tijd (rood) in functie van de peaking time. De standaard fout op de resolutie ligt tussen 0,2 en 0,5 eV. De zwarte verticale lijn ligt op PT = 2 µs. De optimale PT voor geautomatiseerde routinemetingen is 3 µs.

Bij lage PT, is de energie resolutie redelijk slecht, met waarden boven de 170 eV. Na de zwarte verticale lijn is de energie resolutie significant beter en de laagste resolutie wordt bereikt na 30 µs (125 eV). Als nadeel ziet men dat de dode tijd toeneemt naarmate de PT vergroot. Voor geautomatiseerde routine metingen wordt er geopteerd voor een korte PT (3 µs), met redelijke energie resolutie (150 eV) en dus ook een lage dode tijd. Bij metingen waar energie resolutie een hoofdrol speelt zal er voor een hogere PT geopteerd moeten worden.

De bijkomende parameter die een invloed heeft op de energie resolutie is *minimum gap time* (MGT). Deze parameter wordt verondersteld groter te zijn dan de preamp rise time, waarvoor de vaste waarde van 0,6 µs werd genomen. In Figuur 3 wordt dit duidelijk zichtbaar.
waardoor de energie resolutie beter wordt na een waarde van 0,6 µs. De dode tijd stijgt met een procent en is hier van ondergeschikt belang.

Figuur 3: De energie resolutie en dode tijd in functie van de minimum gap time. De waarde 0,6 µs wordt beschouwd als optimaal.

De laatste parameter die een grote invloed heeft op de energie resolutie is de baseline average sample. Wanneer het aantal baseline average samples wordt opgevoerd, daalt de energie resolutie significant voor een PT van 3 µs, bij hogere en lagere PT is deze trend minder uitgesproken, een optimale waarde is 2048. De dode tijd blijft constant voor de bij veranderlijke baseline average sample en is dus geen limiterende factor.

Figuur 4: De energie resolutie (links) en de dode tijd (rechts) in functie van de baseline average sample. De baseline average sample waarde 2048 blijkt optimaal.

**Throughput curve in functie van de telsnelheid**

Throughput wordt gedefinieerd als de verhouding tussen inkomende en uitgaande telsnelheid (ICR en OCR). De relatie tussen de ICR en OCR voor enkele vooraf geselecteerde PT wordt getoond in een throughput curve (Figuur 5). Bij lagere telsnelheden bestaat er een lineair verband tussen de ICR en OCR. Wanneer men kijkt bij lage PT geldt dit verband ook
bij hogere telsnelheden, bij hogere PT krijg je een afwijking van dit verband. Ook bij de lage PT zal deze afwijking voorkomen, maar enkel als de ICR verhoogd wordt. Wanneer de ICR stijgt en de OCR niet meer, zal de dode tijd en dus de analysetijd, sterk vergroten. Dit kan men vermijden door een lagere PT te kiezen, met verlies van energie resolutie, of door de ICR te verlagen. Wanneer de lijn van 3 µs wordt gevolgd zien we dat het lineair verband tussen ICR en OCR geldig blijft, ook bij een telsnelheid van 9000 tps.

Figuur 5: Een throughput curve die het verband tussen inkomende en uitgaande telsnelheden aantoont voor een aantal geselecteerde peaking times. Bij een PT van 3 µs is het lineair verband geldig over het volledig, getoond bereik van de grafiek.

Piek positie in functie van preamp gain, MCA bin width en kanaalnummer

De parameter met de grootste invloed op de piek positie is de gain. De MicroXRF heeft twee verschillende gains, die omgekeerd evenredig met elkaar in verband staan; deze zijn de preamp gain en de MCA bin width. Wanneer de preamp gain verhoogt van waarde moet de bin width verlaagd worden om elkaar te compenseren. Figuur 6 (links) toont de invloed van de bin width op de piek positie in het spectrum.

Ook het aantal kanaalnummers heeft invloed op de piek positie. Naarmate men meer of minder kanalen gebruikt, zullen de kanaalnummers die instaan voor de Fe-Kα piek verschillen. Figuur 6 (rechts) toont deze invloed voor 2048 (rood) en 8192 (zwart) kanaalnummers. De combinatie van het kanaalnummer met de MCA bin width mag nooit de waarde van het dynamisch bereik overschrijden. Bij de MicroXRF is de waarde van het dynamisch bereik 19983 eV.
Figuur 6: Illustratie van de invloed van de *MCA bin widths* (links) en het kanaalnummer (rechts) op de spectrale respons getoond aan de hand van metingen op de ijzerfolie. Broninstelling: 40 kV en 0,5 mA, gemeten voor 100 s LT.

**Thresholds**

De MicroXRF heeft drie thresholds die aangepast kunnen worden: de *trigger threshold* (TT), de *baseline threshold* (BT) en de *energy threshold* (ET). Deze parameters zijn nauw met elkaar verbonden; er wordt aangeraden om eerst de trigger threshold te optimaliseren vooraleer de andere thresholds aangepast worden.

De invloed van de TT wordt onderzocht door de BT uit te schakelen (door de waarde op 0 zetten). Bij lage waarden wordt er een *zero energy noise peak* verkregen (Figuur 7, links), deze soort piek komt voor wanneer ruis beschouwd wordt als een X-straal puls, ook zijn er bij deze waarden geen verstrooingspieken te zien. Naarmate de TT waarde stijgt, zal de zero energy noise peak verdwijnen en worden de verstrooingspieken correct weergegeven (Figuur 8, links). Bij hoge TT worden echter de lage energie pulsen niet meer weergegeven en zal bijgevolg de ijzerpiek uiteindelijk ook worden afgesneden (Figuur 7, rechts). Een ideale waarde voor de TT zal bijgevolg één zijn die de verstrooingspieken correct weergeeft en waarbij geen zero energy noise peak te zien is. De TT moet altijd aangepast worden wanneer de *preamp gain* wordt veranderd; een lagere *preamp gain* waarde zal een hogere TT vereisen. In het geval van de ijzerfolie, bij een peaking time van 3 µs en een preamp gain van 3,5 mV/keV, is de optimale waarde voor de TT gelijk aan 800 eV.

De geoptimaliseerde waarde voor de BT wordt behouden en een ideale waarde voor de BT wordt bepaald. Wanneer de waarde van de BT verhoogd wordt zal de zero energy noise peak terug verschijnen. Het is belangrijk om te benadrukken dat een zero energy noise peak absoluut moet vermeden worden, met deze piek bestaat de kans dat de detector inconsistent reageert, met betrekking tot de dode tijd, dewelke de meting beïnvloedt. Verder verhogen van de BT zal de lage energie signalen afsnijden (Figuur 8, rechts). Daarom wordt de BT geoptimaliseerd aan de hand van een monster dat een element bevat met laag atoomnummer (b.v. Al). De waarde waarbij deze piek nog volledig te zien is, is de geoptimaliseerde baseline threshold waarde. Telkens wanneer de *preamp gain* of de PT wordt gewijzigd, moet de BT opnieuw geoptimaliseerd worden. In het geval van de ijzerfolie, bij een peaking time van 3 µs en een preamp gain van 3,5 mV/keV, is de optimale waarde voor de BT gelijk aan 700 eV.
Er wordt aangeraden om de *energy threshold* in de meeste gevallen uit te schakelen, omdat er een kans bestaat dat een statistische fout wordt geïntroduceerd\textsuperscript{[21]}. Dit werd dan ook gedaan voor de MicroXRF.

Figuur 7: Illustratie van de invloed van de *trigger threshold* op het XRF spectrum getoond aan de hand van de ijzerfolie, links heeft de TT een lage waarde (50 eV), rechts een hoge (2500 eV). Broninstelling: 40 kV en 0,5 mA, gemeten voor 100 s LT.

Figuur 8: Illustratie van de invloed van de *thresholds* op het XRF spectrum getoond aan de hand van de ijzerfolie, links worden de gereduceerde verstrooingspieken getoond door de TT te wijzigen en rechts wordt de lage energie afsnijding getoond bij verhogen van de BT. Broninstelling: 40 kV en 0,5 mA, gemeten voor 100 s LT.

Overzicht van de geselecteerde detector parameter waarden gebruikt voor geautomatiseerde routine metingen

Tabel I geeft een overzicht van de experimenteel bepaalde optimale waarden voor de verschillende detector elektronica parameters, die toelaten om routine metingen geautomatiseerd uit te voeren met behoud van de nodige spectrale kwaliteit. De invloed op de analytische kenmerken op de het XRF spectrum is ook aangeduid. Voor de ijzerfolie geeft deze combinatie van detector parameters een energie resolutie van 150 eV voor de Fe-\( \text{K}_\alpha \) piek en een dode tijd van 5% bij een gemiddelde telsnelheid van 5000 tps.
TABEL I: Samenvatting van de geselecteerde parameters voor een geautomatiseerde routine meting. De polariteit, reset interval en preamp rise time hebben een vaste waarden en hun invloed op de spectrale respons werd niet onderzocht.

<table>
<thead>
<tr>
<th>Detector parameter</th>
<th>Invloed op</th>
<th>Waarde</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polariteit</td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>Reset interval (µs)</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Preamp rise time (µs)</td>
<td></td>
<td>0,6</td>
</tr>
<tr>
<td>Peaking time (µs)</td>
<td>PT</td>
<td>3</td>
</tr>
<tr>
<td>Minimum gap time (µs)</td>
<td>MGT</td>
<td>0,6</td>
</tr>
<tr>
<td>Baseline average sample</td>
<td>BAS</td>
<td>2048</td>
</tr>
<tr>
<td>Preamp gain (mV/keV)</td>
<td></td>
<td>3,5</td>
</tr>
<tr>
<td>MCA bin width (eV/bin)</td>
<td>Piek positie</td>
<td>9,72</td>
</tr>
<tr>
<td>Aantal kanaalnummers</td>
<td></td>
<td>2048</td>
</tr>
<tr>
<td>Dynamic range (keV)</td>
<td></td>
<td>19.983</td>
</tr>
<tr>
<td>Trigger threshold (eV)</td>
<td>TT</td>
<td>800</td>
</tr>
<tr>
<td>Baseline threshold (eV)</td>
<td>BT</td>
<td>700</td>
</tr>
<tr>
<td>Energy threshold (eV)</td>
<td>ET</td>
<td>0</td>
</tr>
</tbody>
</table>

Conclusie

Het doel van dit werk was om een ideale combinatie van detector parameters te vinden voor de nieuwe XMI MicroXRF spectrometer, die nuttig kunnen zijn voor geautomatiseerde en routinematig uitgevoerde metingen. Dit werd gedaan via de studie van de invloed van de detector parameters op de kwaliteit van het spectrale respons door de kijken naar energie resolutie, throughput, piek positie en de correcte weergave van de lage energie en verstrooiingspieken.

De energie resolutie wordt vooral beïnvloed door de peaking time: wanneer hogere waarden van deze parameter geselecteerd werden, bekwam men een hogere energie resolutie. Dit resulteerde in een hogere dode tijd en dus langere analysetijd. Voor routine metingen werd er geoptereerd voor een lagere peaking time (3 µs), deze heeft een veel lagere dode tijd, maar kan toch nog een goede energie resolutie (150 eV) voorleggen. Andere factoren die de energie resolutie bepaalden zijn de minimum gap time en baseline average sample, die werden geoptimaliseerd voor de best haalbare spectrale energie resolutie.

De piekpositie werd voornamelijk bepaald door twee verschillende gains, de preamp gain en MCA bin width. Deze parameters waren nauw met elkaar verbonden en de beste combinatie van deze parameter waarden werd gekozen.

De optimale waarden voor verschillende thresholds; de trigger, de baseline - en de energy threshold werden bepaald. Bij het optimaliseren is het belangrijk om de zero energy noise peak te vermijden omdat, wanneer deze piek verschijnt, de detector inconsistent kan reageren met betrekking tot de dode tijd en dus de meting kan beïnvloeden. Het is belangrijk dat de verstrooiingspieken correct worden weergegeven en dat pieken van lage Z elementen volledig zichtbaar zijn.

Een overzicht van de experimentele bepaalde optimale waarden voor de verschillende detector elektronica parameters, die toelaten om routine metingen geautomatiseerd uit te voeren met behoud van de nodige spectrale kwaliteit, werd getoond in Tabel I. Hoewel deze
parameters hier enkel werden geoptimaliseerd door een ijzerfolie te analyseren, zijn deze waarden ook toepasbaar op andere soorten materialen zoals blijkt uit metingen op andere standaarden (resultaten niet getoond in dit werk).

Referenties


