

## Instrument Parameters (Part 2)

Pol De Pape, XRF Application Scientist, Rigaku Latin America

### 1. Introduction

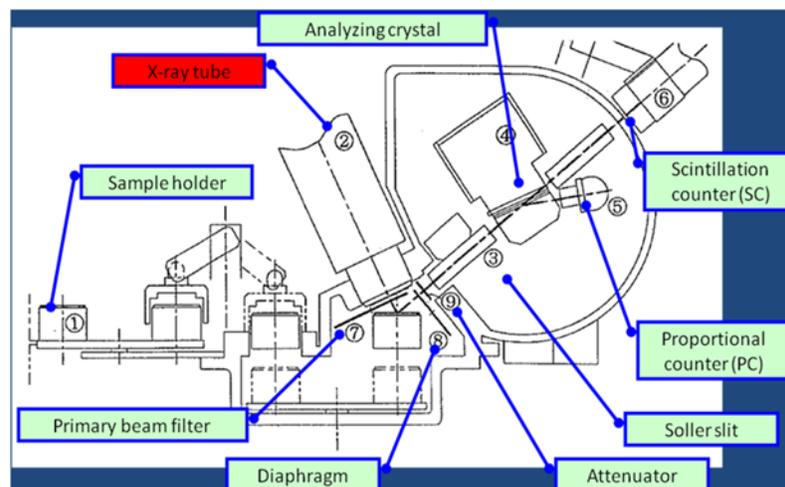
In the previous article, we learned about the basics of X-ray fluorescence as a spectroscopic analysis technique. We saw that it is a technique that has been established for many decades and has a wide range of applications. It also explained the basic principles or physics of X-rays.

In this article, we will apply those principles to the hardware and, in particular, to the X-ray tube of an (wavelength dispersive) X-ray spectrometer.

### 2. Outline of a WD-XRF spectrometer

WD-XRF stands for **W**avelength **D**ispersive **X-Ray** **F**luorescence, which means that we are going to separate the elements we want to analyse by wavelength. The hardware within an XRF instrument that does this is the analysing crystals.

Nevertheless, before we can start separating elements, we need to create X-rays. Primary X-rays, i.e. photons that we will use to excite the sample we want to analyse, are created in the X-ray tube. The primary X-rays will impinge on our sample and subsequently produce secondary X-rays. Because these X-rays scatter in all directions, they are sent through a Soller slit (collimator) to create a parallel X-ray beam that can be much more easily reflected by the crystals. After diffraction by the crystals, the X-ray photons move towards the detector for the element's energy, where photons are translated into a measurable electrical pulse.



WD-XRF layout

This diagram shows an example of the outline of an XRF spectrometer. Some parts may be different from the current models, like ZSX Primus and the ZSX Primus IV, where the scintillation detector is inside the vacuum chamber. Also, the X-ray tube is not always on top of the sample. The sample can also be irradiated from below, which would be most practical when mainly liquid samples are measured.

### 3. The X-ray tube

The purpose of the X-ray tube is to provide a highly intense beam of X-rays with a wide band of wavelengths (energies) with which the elements present in the sample (that is to be analyzed) can efficiently be excited.

Three parameters of the X-ray tube design are of primary importance in achieving this:

- a. Anode material: defines which elements or group of elements can more readily be excited. A light-element anode (Cr) would excite lighter elements. A heavier element anode (W, Au) would excite heavier elements. An anode that makes it possible to excite almost all elements, and which is therefore most frequently used, has a rhodium (Rh) anode.
- b. Window material and thickness: the tube window must be made of material that barely absorbs the primary X-rays and which is still very stable under extreme (heat) conditions. Therefore, beryllium<sup>4</sup> is the most convenient metal. The thinner an X-ray tube window is, the easier the lighter energies will leave the tube. This means that more primary photons are available for excitation (of the light elements). Consequently, the sensitivity of those elements increases drastically. A good example is the ZSX Primus IV WD-XRF, which has an X-ray tube window of just 30µm. The higher energies, which will excite heavier elements, are barely absorbed by Be. In this case the window thickness doesn't play a big role.
- c. Excitation conditions (kV and mA settings): the higher the power that is available, the more sensitively we can analyze the elements of interest. Tube power can vary from a few Watts to a few 1000s of Watts. The power of the X-ray tube is divided between a variable voltage (mostly expressed as kV) and a variable current (mostly expressed as mA). A general rule of thumb is: "Higher atomic number elements need more kV; lighter elements need more mA." More explanation about the use of kV and mA will be given further in this article.

Other considerations for the X-ray tube are:

- a. Design (end- or side- window): today the end window design is mostly used because the anode-to-sample distance becomes shorter and therefore the efficiency increases. Nevertheless, with a side window design higher kV (up to 100 – 120kV) can be reached and, therefore, higher energies can be excited, which makes it easier to analyze, for example, the Lanthanide group elements.

In the case of the side-window tube, the electrons reflected on the target strike the Be window and, therefore, the Be window must be thick. Otherwise, the Be window does not last long owing to damage by the electrons.

- b. Cooling efficiency: the efficiency of an X-ray tube is actually very poor. Most of the energy created (>95%) is lost as heat. Therefore, cooling an X-ray tube is very important. Otherwise, the tube would burn out within minutes. Lower power tubes (<200W) can be cooled with air. Higher power tubes need water cooling. Some designs can do the cooling with only an internal water circuit for cooling down the back of the anode. Other models (>2kW) will also need an external water cooling for additionally cooling the tube housing.

- Window material: Be 30 – 1000  $\mu\text{m}$
- Tube power = composed of excitation potential (kV) and current (mA)
  - Production of primary X-rays
  - Depends on the element's electron binding (ionization) energy
    - High energy: high kV
    - Light energy: high mA
- Cooling by internal and/or external water circuit
  - 50W – 1kW systems: air cooled or only internal water for anode
  - 2.4kW - 4kW spectrometer: cooling anode and tube housing by internal cooling water from heat exchanger

Type	Target Material	Grounding	Window Thickness	Max. load	Cooling water
Side-window	W, Cr, Mo, Au, etc.	Anode	1000 $\mu\text{m}$ , 300 $\mu\text{m}$ (Cr)	2.4 - 3kW	Tap water
End-window	Rh, Pd, etc.	Cathode	127 - 30 $\mu\text{m}$	0.05 - 4kW	Deionized water

X-ray tube - Overview

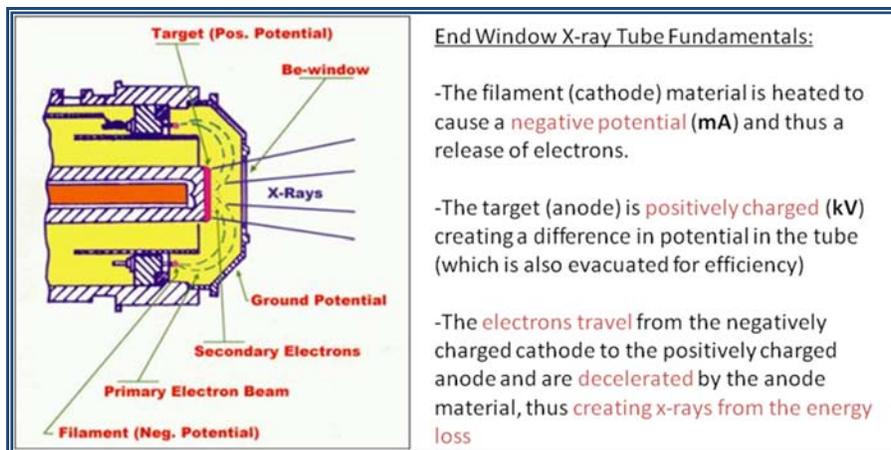
#### 4. How the end window tube functions

The cathode (W-filament) of the X-ray tube is heated by a current (mA) to cause a negative potential. A negative potential means the release of electrons, and the higher the current used, the more electrons will be produced. In the case where light elements, which are not highly sensitive to X-rays, need to be excited, a high current will be beneficial.

The anode or target (metal) of the X-ray tube is positively charged (kV), creating a difference in potential.

The electrons travel from the cathode to the anode. The higher the applied kV is, the stronger the electrons (created in the cathode) will be attracted towards the anode. Once the electrons strike the anode they will decelerate and will release a wide band of energies (the white spectrum or Bremsstrahlung) coming from the loss in energy.

The X-ray tube is evacuated to improve efficiency.



End window tube

## 5. Origin of X-rays

When high-energy electrons interact with matter, two distinct types of radiation will be observed:

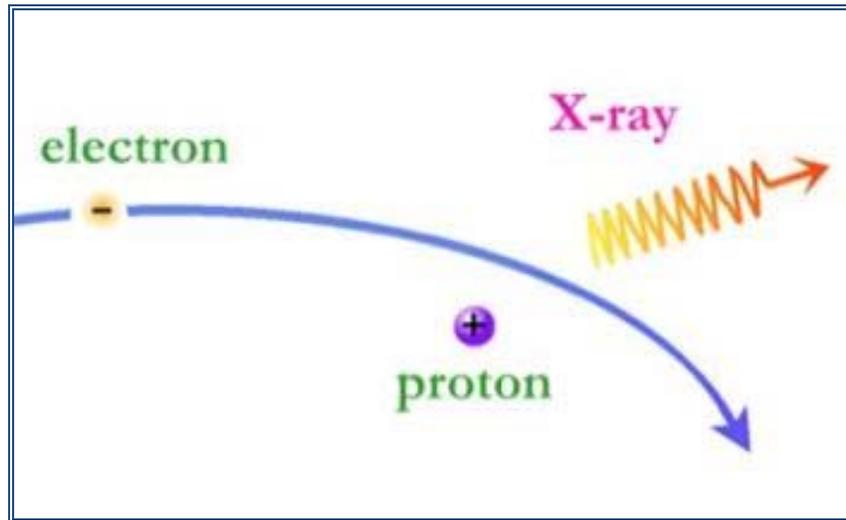
- a. Continuum or white radiation or Bremsstrahlung: when a high-energy electron beam is incident upon a specimen, one of the products of interaction is an emission of a broad wavelength band. This continuum is produced as the impinging high-energy electrons are decelerated by the atomic electrons of the elements making up the specimen.
- b. Characteristic radiation: When a high-energy particle, such as an electron or a photon, strikes a bound atomic electron, and the energy  $E$  of the particle is greater than the binding energy  $E_b$  of the atomic electron, the atomic electron may be ejected from its atomic position. In this way the atom becomes unstable and a re-arrangement of the electrons subsequently occurs. Characteristic radiation arises from the energy transfers involved in the re-arrangement of orbital electrons of the target element, following ejection of one or more electrons in the excitation process. The ejected electron in this process is called the photoelectron and the interaction is called the photoelectric effect. Characteristic radiations are discrete wavelengths, which depend on the atomic number of the element.

- In the following slides, the different types of radiations and effects caused by electrons or photons, relevant to the analysis by XRF, will be explained
- X-rays originate from the energy loss associated with the interaction of high energy electrons or X-rays with atoms
- The spectrum of an X-ray tube shows two types of X-ray radiation
  - **Bremsstrahlung** = Continuous radiation or white radiation
  - **Characteristic radiation** = Unique energies to anode elementBoth types of radiation depend on the anode material

*Types of radiation*

## 6. Bremsstrahlung

Comes from the German word “bremsen” (decelerate or braking) and “Strahlung” (radiation). It is the electromagnetic radiation that occurs as a charged particle, for example an electron, is decelerated around the nucleus of an atom. Each change in velocity or deviation in direction creates radiation. The range of changes is large and therefore the spectrum is very broad (Bremspectrum).



*Bremsstrahlung: principle*

Kramer's formula is applied for the calculation of the Bremsstrahlung

- I = intensity at wavelength □
- K = constant
- i = current (mA)
- Z = atomic number of the anode
- $\lambda$  = wavelength of Bremsstrahlung
- $\lambda_{\min}$  = Lower wavelength limit for applied voltage

$$I(\lambda) = KiZ \left[ \frac{\lambda}{\lambda_{\min}} - 1 \right] \left[ \frac{1}{\lambda^2} \right] \quad \lambda_{\min} = \frac{h.c}{kV}$$

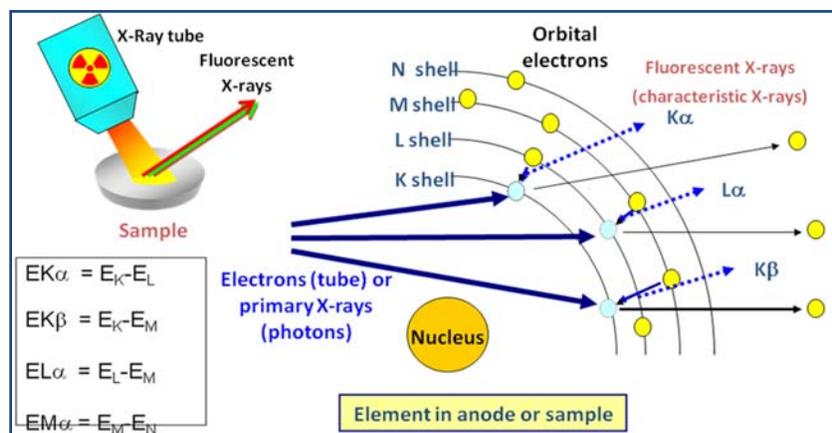
Kramer's formula shows that the intensity of the continuum  $I(\lambda)$  is proportional to the atomic number ( $Z$ ) of the anode material and that, therefore, in principle, the higher the atomic number of the anode the better. The intensity will also depend on the applied current ( $i$ ), where a linear relationship exists, and the applied tension ( $kV$  related to the wavelength  $\lambda$ ). However, the conversion of electrons to X-rays is a very inefficient process, with only about 1% of the total applied power emerging as X-rays. The remainder of the energy appears as heat, much of which must be dissipated by the anode, and from this point of view the anode must also be a good heat conductor. Also, therefore, high-power X-ray spectrometers do need an extensive cooling circuit.

## 7. Characteristic X-rays - Principle

Characteristic X-rays generated by incident X-rays are called *fluorescent X-rays*. The primary X-rays from the X-ray tube are irradiated onto the sample and fluorescent X-rays are excited.

The right part of the figure below explains the excitation of fluorescent X-rays using the Bohr atom model. When the primary X-rays hit a K shell electron, electrons are kicked out (photo electrons) and move toward the conduction band of the atom. Subsequently, electrons from the outer shells shift down onto the K shell to stabilize the atom again, releasing an energy that is the difference between the binding energy of the K electron with the electron that falls into the vacancy. For example: when an L-shell electron shifts onto the K shell, fluorescent X-rays with the energy equivalent to the difference in energy level between the K shell and the L shell are generated. These are called K-alpha ( $K\alpha$ ) lines.

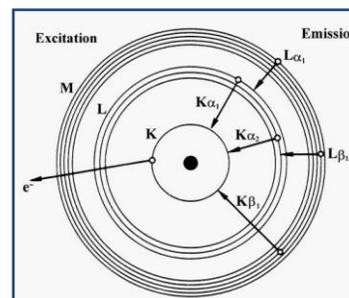
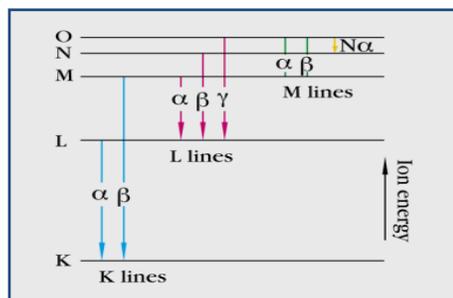
The wavelength (or energy) of the fluorescent X-rays is unique for the element. The line name is defined by which shells the electron shifts from and to.



## 8. Nomenclature of X-rays

The illustrations below show a few ways to name the characteristic lines, where the electrons originate from and where they end up. The ion energy increases as we move to outer shells/orbitals.

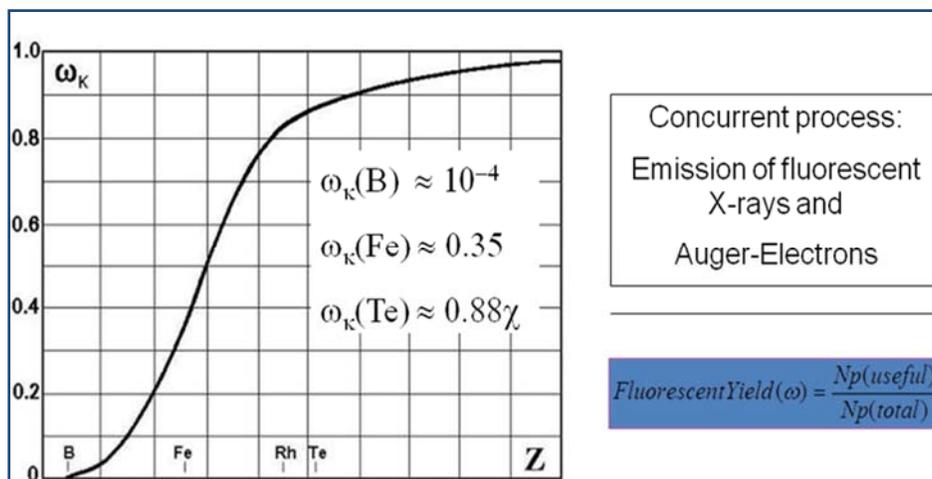
The more electrons an atom possesses, the more electron transitions can take place and subsequently the more characteristic lines can be detected. Nevertheless, the most commonly detected transitions are  $K\alpha$ ,  $K\beta$ ,  $L\alpha$ ,  $L\beta$ ,  $M\alpha$  and  $M\beta$ . The characteristic lines will also get an index (e.g.  $K\alpha_1$ ) to show from which exact energy level the substituting electron comes from.



## 9. Fluorescent Yield

It has been pointed out that the extra energy that an atom possesses after an electron jump, for example L to K, may be emitted as characteristic radiation. Alternatively, this energy may lead to the ejection of one or more electrons from the outer shells. The probability of this type of ionisation increases with the decrease in the difference of the corresponding energy states. For example, when  $(E_K - E_L)$  is only slightly larger than  $E_L$ , this ionisation probability is large. This means in turn that only in a small number of the total original K ionisations is the energy emitted as K radiation. This phenomenon is called the *Auger effect*. Practically, lighter elements will give rise to more Auger electrons than heavier. This explains the lower sensitivity for lighter elements!

An important consequence of the Auger effect is that the actual number of X-ray photons produced from an atom is less than would be expected, since a certain fraction of the absorbed primary photons gives rise to Auger electrons. The ratio of the useful X-ray photons,  $N_p$  (useful), arising from a certain energy shell to the total number of primary photons,  $N_p$ (total) absorbed in the same shell, is called the *Fluorescent Yield ( $w$ )*.



Fluorescent yield

## 10. Compton- and Thomson (Rayleigh) scattering

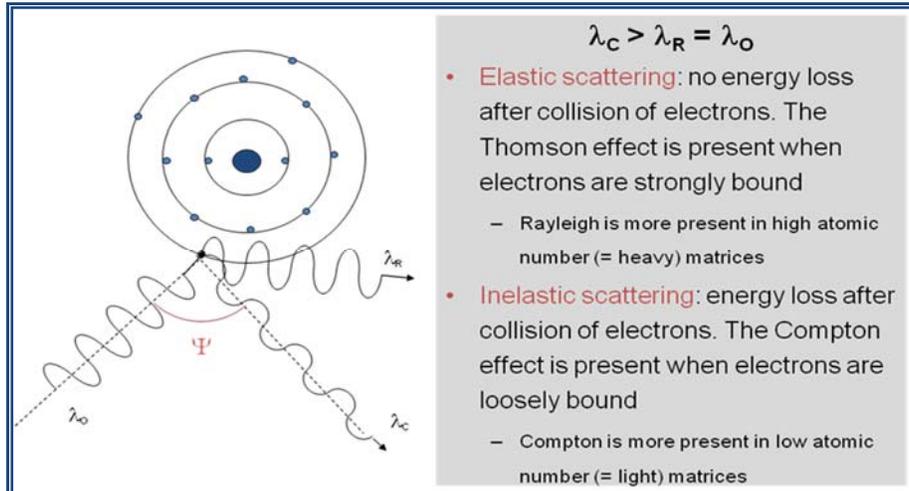
Two types of scattering take place: coherent and incoherent, also known as Thomson (Rayleigh) and Compton scattering.

Coherent scatter arises when an X-ray photon collides with an electron and is deflected without loss of energy, the corresponding wavelength remaining unchanged.

If the electron is only loosely bound, the colliding electron may lose part of its energy to the electron. As the energy of the scattered photon has decreased we talk about incoherent scatter.



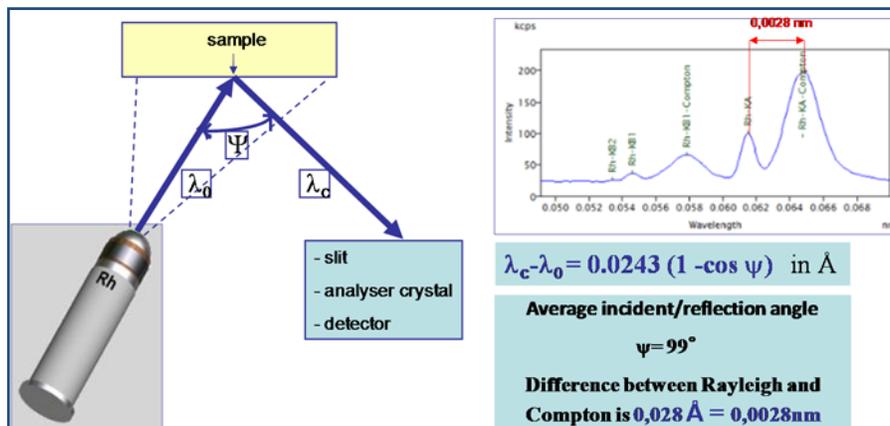
Arthur Holly Compton



*Scattering effects*

The relationship between the incoherent scatter ( $\lambda_c$ ) and the incident wavelength ( $\lambda_0$ ) is:

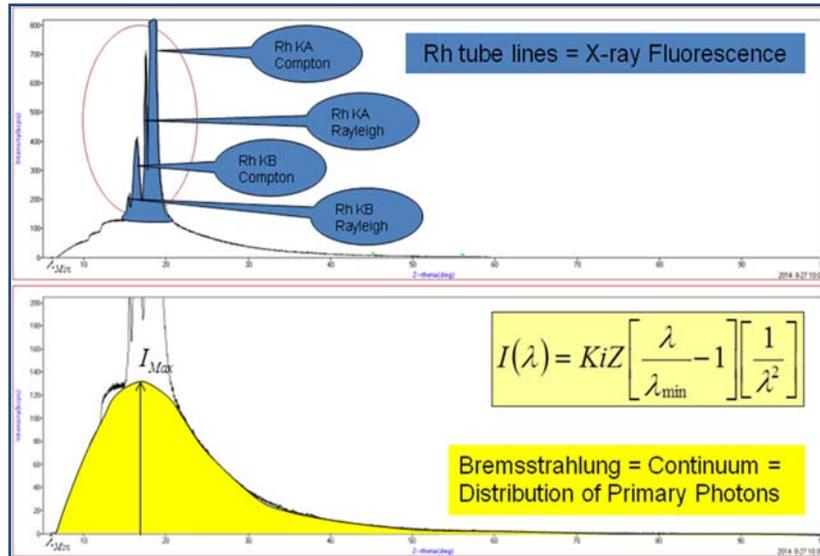
$\lambda_c - \lambda_0 = 0,0243 * (1 - \cos\psi)$ , This makes it possible to calculate the exact distance (in a spectrogram) between the two peaks.



*Compton and Rayleigh*

## 11. The X-ray tube spectrum

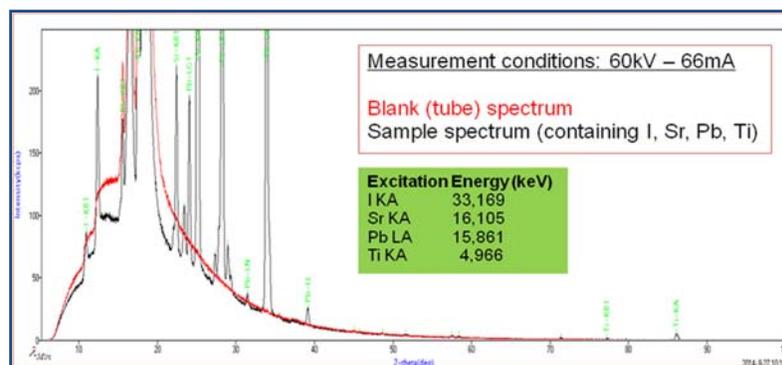
We can now summarize all of the above described effects in an X-ray tube spectrum; or, in other words, what we can see as the output from an X-ray tube. The spectrum is actually a distribution of energies or photons. The higher the spectrum's intensity is, the more photons are available or the more efficiently elements with energies, at that position, can be excited. One can see that at higher 2-theta positions fewer photons are available. This is also a reason why lighter elements are more difficult to analyze.



X-ray tube spectrum

## 12. Secondary (sample) radiation

With the energies leaving the X-ray tube, we will be able to excite the sample we would like to analyse. In order to demonstrate the effect of X-rays on different energy elements, an artificial sample was created containing equal quantities of I, Sr, Pb and Ti in boric acid. The elements were excited with exactly the same conditions: 60kV and 66mA. A comparison between a blank boric acid sample and the artificial sample was made. We can clearly see a lower spectrum for the sample containing the elements. This is due to the absorption of X-rays by matter. Also, the lighter an element gets, the lower the sensitivity (peak height) will be. This is explained by the presence of fewer primary photons. One can also observe that Iodine loses intensity compared to Sr and Pb. This is because 60kV is not enough kV to excite Iodine ideally. As Pb has many electrons, many transitions (peaks), with varying intensities, can be seen. The appearance of peaks is a probability distribution or not all transitions are equally present. A  $K\alpha$  peak is generally higher in intensity than a  $K\beta$ , or  $K\alpha$  is more present than  $K\beta$ . But this depends also on the elements we're looking at;  $K\alpha/K\beta$  ratios can vary from 20/1 to 1/1 or even 1/2.



Sample spectrum

### 13. Influence of kV and mA

We have seen before that the X-ray tube's output is driven by the parameters kV and mA (voltage and current). Let's assume we have an operational power of 4kW (4000W). The power is the product of the voltage and current:  $P = U * I$  or  $4000W = U * I$ .

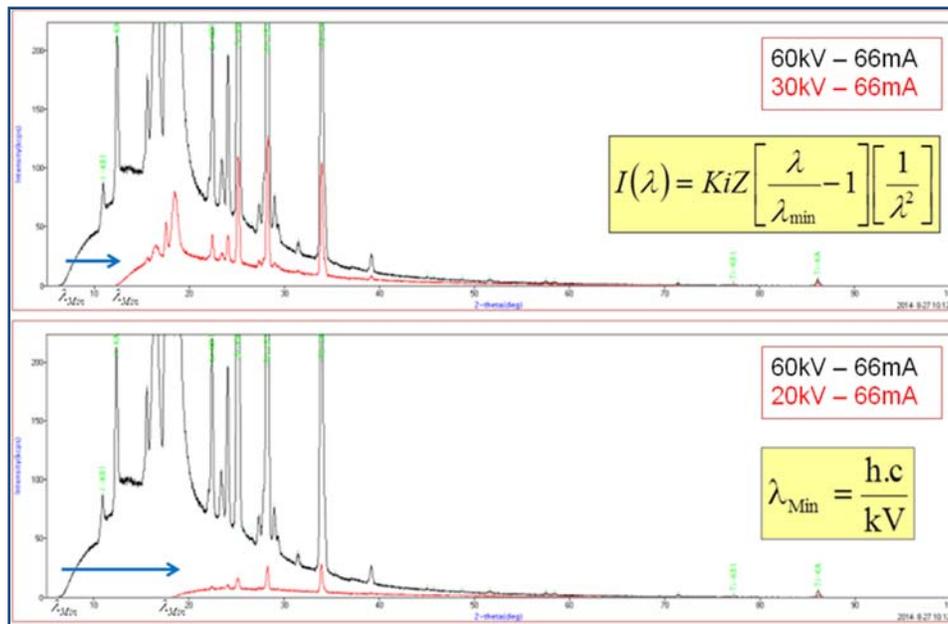
We can now distribute this power between U and I, but we have to keep in mind that the maximum potential is 4000W. When we apply, for example, 60kV, the maximum current we can use would be 66mA. Otherwise, when we apply 100mA, the maximum voltage we can use will be 40kV. We have thus a lot of flexibility between the minimum and maximum settings of both kV and mA, but the multiple is always restricted to the maximum power of the X-ray tube.

Depending on the power of the X-ray tube (1W to 4200W), we will have the possibility to excite elements according to the available mA and kV. When the power of an X-ray tube is low; generally the voltage may be up to 30 – 50kV, but the current will only be in the range of  $\mu A$  to a few mA; a principle mostly used by ED-XRF spectrometers. This principle makes ED-XRF much less sensitive for lighter elements.

When the kV is decreased and the mA is kept stable, the minimum wavelength that can be excited will shift towards higher 2-theta angles or certain K electrons, such as for the elements Iodine or Strontium in our example, cannot be excited anymore.

Decreasing the kV also shows that the intensity output (or the sensitivity = possibility to analyze elements) gets much lower.

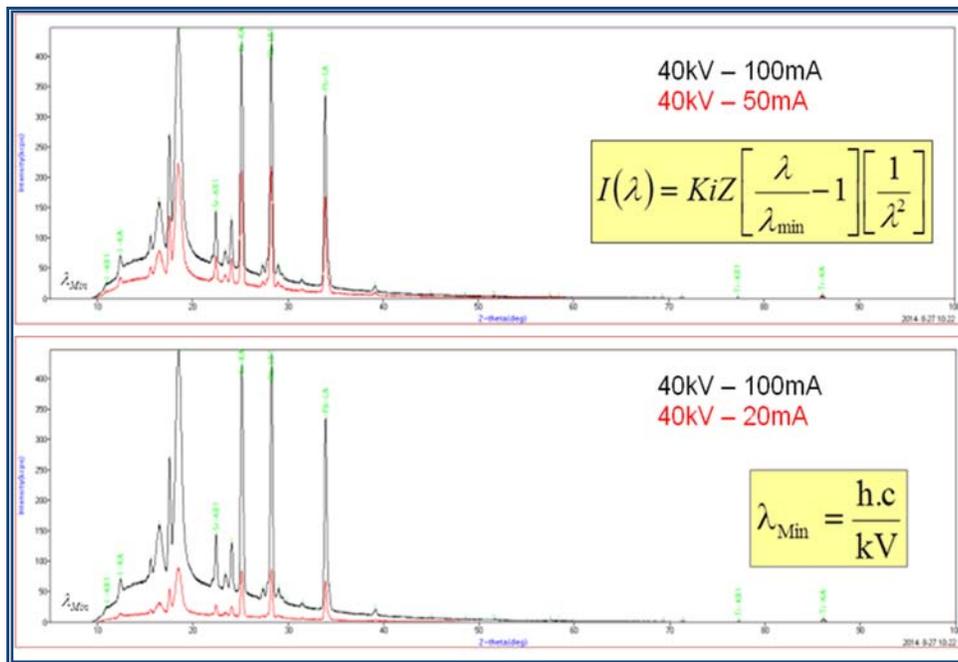
This example proves that, when high atomic number elements are of importance or where electrons are strongly bound, high kV is a must.



Influence of kV

When now the kV is kept stable and the mA is getting changed, one can see that the  $\lambda_{\min}$  doesn't change anymore but the intensity (sensitivity) changes linearly with the current (see also Kramer's formula). In other words, when the current decreases by a factor two, the spectrum will become a factor two lower or two times fewer photons will be available.

In case of the analysis of light elements, we will thus prefer to use a high mA with low kV, as we need as many primary photons (which do not need to have a high energy) as possible. Light elements are namely not sensitive as we had also seen from the fluorescent yield graph.



Influence of mA