Total Reflection X-ray Fluorescence Analysis.

Section 2

2. Instrumentation (spectrometer)

TXRF is a rather cost-effective method for multi-elemental analysis. The principle of work of EDXRF spectrometers is based in sequential processes which need to be understood by the analyst, not only to be able to identify possible failures, but also to improve the performance of the spectrometer.

This section will introduce you to the principles of detection and further processing of the measured signals, up to its final presentation in the form of an x-ray spectrum.

2.1- Spectrometric track

A conventional spectrometric array includes the following modules:
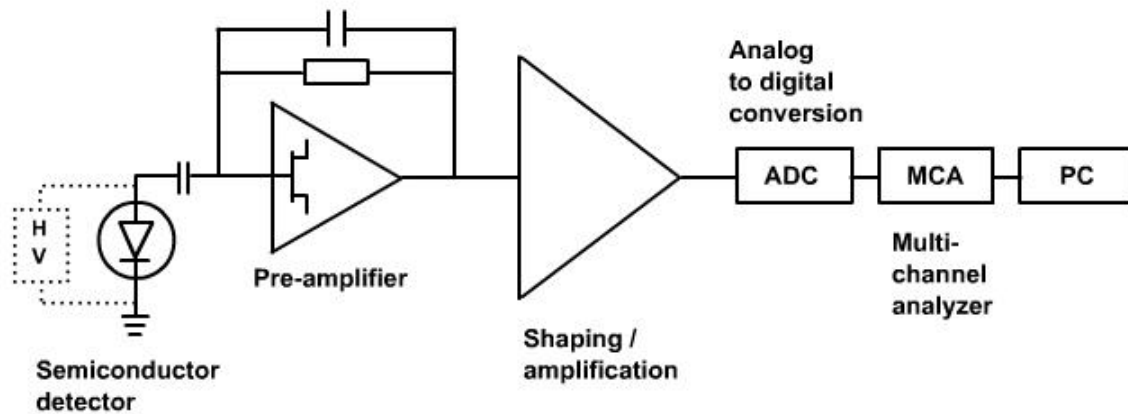
2.1.1- Detectors

The heart of any EDXRS is the solid state semiconductor detector. Two major kinds of detectors are used in TXRF: Si(Li) and Silicon Drift Detectors (SDDs).

- The detector is composed of a non-conducting or semi-conducting material between two charged electrodes.

- X-ray radiation ionizes the detector material causing it to become conductive, momentarily.

- The newly freed electrons are accelerated toward the detector anode to produce an output pulse.

- In ionized semiconductor detectors the x-ray produces electron-hole pairs. The number of such pairs produced is proportional to the X-ray photon energy.

> The mode of operation is similar for both types.

2.1.2- The Si(Li) Detectors Crystal

The Si(Li) Detector Crystal

An incident photon interacts with an atom producing a series of electrons and hole pairs. The pairs are separated under the influence of High Voltage. Thus, a small charge pulse is produced.
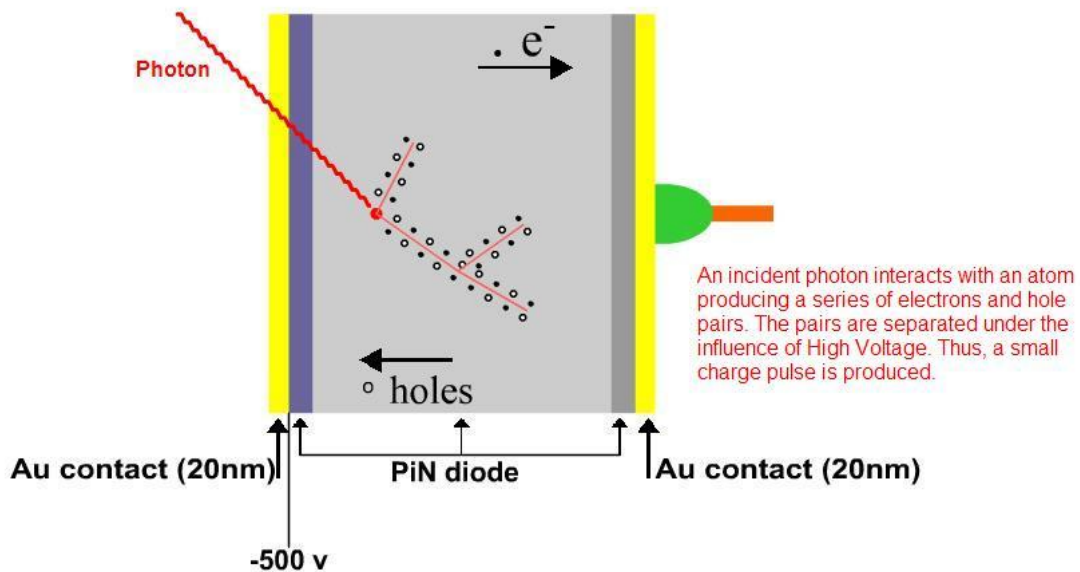
2.1.3- Silicon Drift Detectors (SDDs)

Silicon Drift Detector (SDDs)

Silicon drift detector with an integrated JFET* as a first amplifier. The reverse of the diode and the front side diode rings are used to deplete the detector from mobile charges and to generate a drift field for those electrons which are generated in the silicon bulk by the x ray.

X-rays

p

n

e-

p

An incident photon interacts with an atom producing a series of electrons and hole pairs. The pairs are separated under the influence of High Voltage. Thus, a small charge pulse is produced.

S G D

-V

field strips   **anode**

JFET*

*junction gate field-effect transistor
source, gate, drain

2.1.4- SDD Principle

SDD Principle

$$n_e = h \frac{v}{\varepsilon}$$
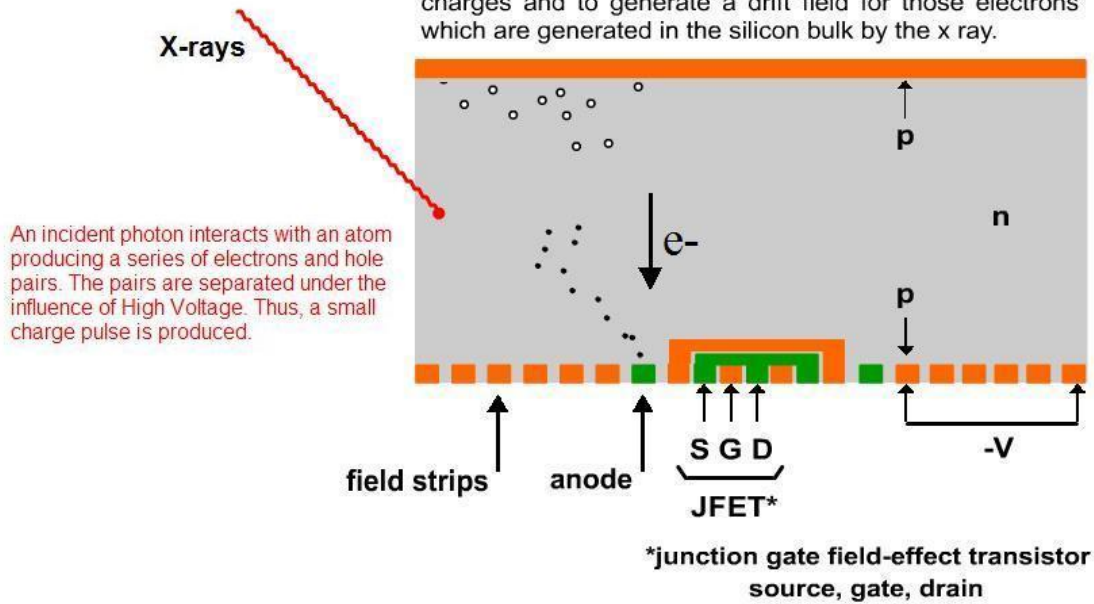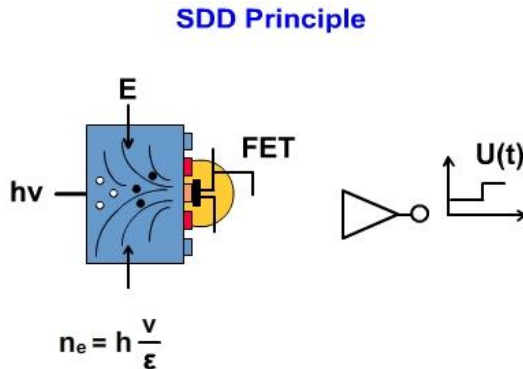
The basic form of the Silicon Drift Detector consists of a volume of fully depleted high-resistivity silicon, in which an electric field with a strong component parallel to the surface drives electrons generated by the absorption of ionizing radiation towards a small sized collecting anode. The electric field is generated by a number of increasingly reverse biased field strips covering one surface of the device. The radiation entrance window on the opposite side is made up by a non-structured shallow implanted junction giving a homogeneous sensitivity over the whole detector area.

The unique property of this type of detector is the extremely small value of the anode capacitance, which is independent of the active area. This feature allows to gain higher energy resolution at shorter shaping times compared to conventional photo diodes and Si(Li) detectors, recommending the SDD for high count rate applications.

To take the full advantage of the small output capacitance the front-end transistor of the amplifying electronics is integrated on the detector chip and connected to the collecting anode by a short metal strip. This way the stray capacitance of the interconnection detector - amplifier is minimized and moreover noise by electric pickup and microphony effects is insignificant. The anode is discharged from signal electrons in a continuous mode. Thus the SDD can be operated with dc-voltages only and there is no detector dead time caused by a clocked reset mechanism.

Due to the elaborated process technology used in the SDD fabrication the leakage current level is so low that the SDD can be operated with moderate cooling by means of a single stage Peltier element.

The SDD's energy resolution (FWHM < 145 eV @ MnKa, -20oC) can be compared to that of a Si(Li) detector requiring no expensive and inconvenient liquid nitrogen cooling. It surpasses the quality of pin-diodes.

To improve performance of the standard Silicon Drift Detector with regard to energy resolution and peak-to-background a new SDD-layout were developed. The integrated FET is no longer centered but moved to the outside margin of the structure. If a proper collimator is used, the FET is not irradiated by incoming photons.

When irradiating silicon drift detectors with high doses of X-rays photons, radiation damages in the oxides and at the interface oxide/silicon occur. The most important effect after irradiation is the increased surface leakage current which leads to a worse energy resolution.

2.1.5- Signal processing

The charge pulses produced by the detector are subsequently processed by a complex electronic system. They are amplified, shaped and sorted according to their amplitudes. Finally all pulses with certain amplitudes are counted. A strong proportionality between the amplitude of the initially produced pulses and subsequently processed pulses should accurately be maintained. As long as this condition is met, the pulse amplitude remains an accurate measure of the energy of the detected photons. Ultimately, the result of the photon counting can be represented as an energy dispersive spectrum representing the number of photons as a function of their energy.
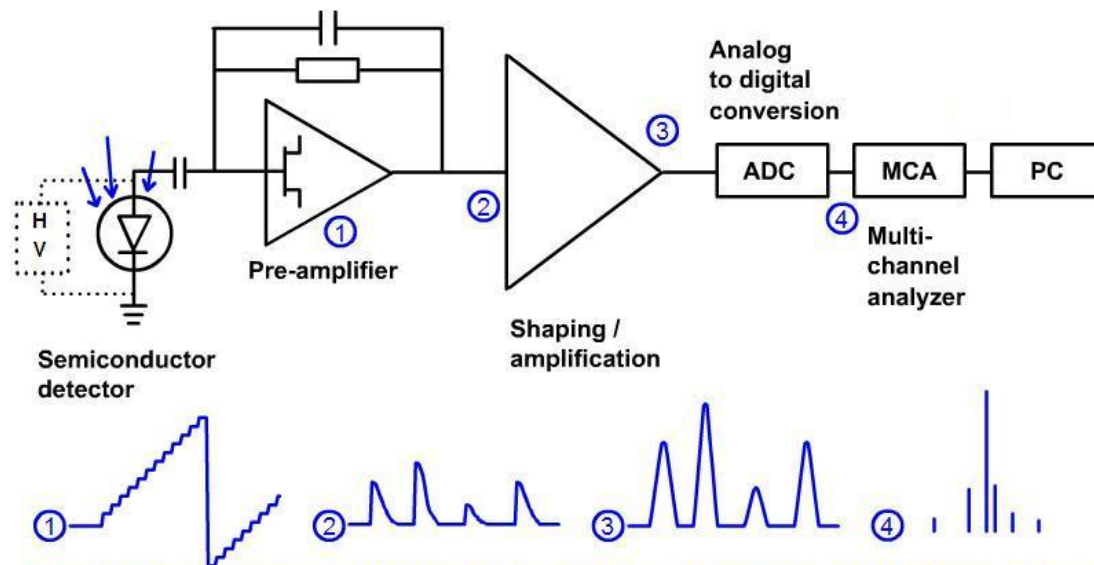

An analog to digital converter (ADC) inspects the amplitude of the pulses and determines a digital code value for each. The reception of a pulse having a specific digital code is registered in a proportional (to that code) channel in the multichannel analyzer (MCA).

2.1.6- Spectra. Escape peaks. Sum peaks.

Escape peaks arise when a strong element peak is recorded. Their formation occurs within the detector crystal. When an incident photon is passing through the detector volume and its characteristic energy is sufficiently high, it can produce a photoelectron from an inner shell of a crystal atom (Si). As a result, the excited atom can emit a fluorescence X-ray photon, mostly a K_α photon. It is most of the times reabsorbed thus contributing to the charge pulse. However, that photon can also escape from the crystal. In that case, it carries off the definite energy of the $Si-K_\alpha$. The charge pulse appear as corresponding to a photon energy $E_{initial} - E_{Si-K_\alpha}$ and therefore show up in the spectrum as separate spurious peaks.

Sum peaks are due to the coincidence of two photons with different energies entering into the detector. Sum peaks are often found when a few large peaks at lower energy dominate the spectrum. It is important to note that the intensity of the sum peaks is count-rate dependent, they can be reduced and virtually eliminated by performing the measurement with lower primary beam intensity.

Synthethic Bronze (XRTube Ag + Rh ST, 40 kV, 10 mA)
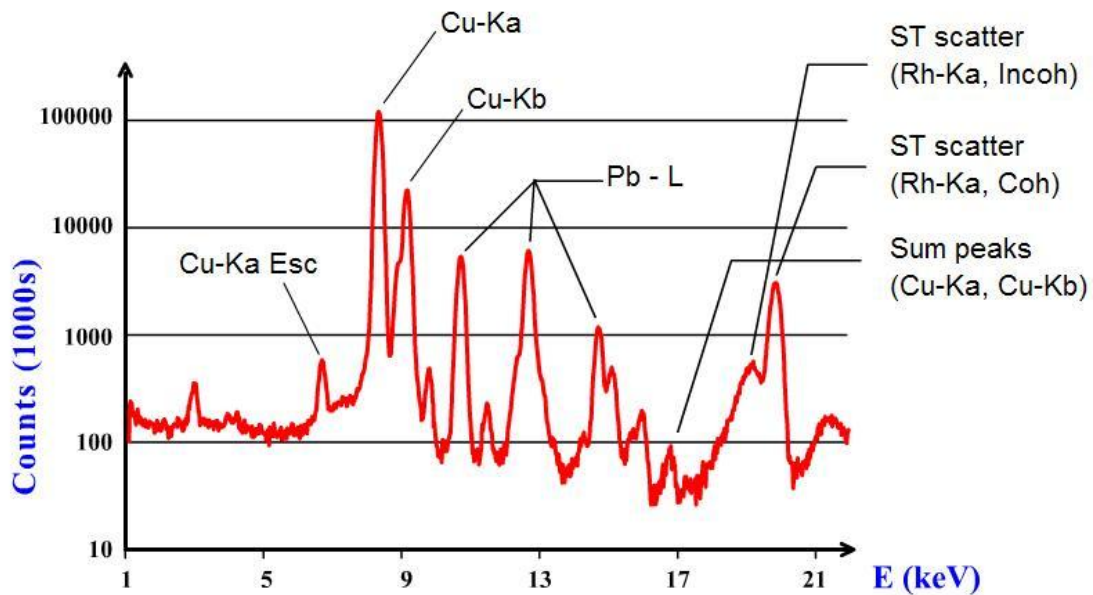
2.1.7- Spectrometer efficiency

Efficiency is defined as the percentage of the detected photons with respect to the amount of incident photons. The efficiency is nearly 100% for energies from 6 to 11 keV but is reduced for lower and higher energies. This lowering is the result of the absorption in the Beryllium window, in the Gold layer and in the inactive layer of the detector, for low energy photons. For high energy photons the transmission though the crystal is the relevant factor.

Detector intrinsic efficiency

Si: 0.5 mm; Be: 25 mm; Au: 30 nm

Si: 3 mm; Be: 12.5 mm; Au: 20 nm

Si: 3 mm; Be: 8 mm; Au: 10 nm
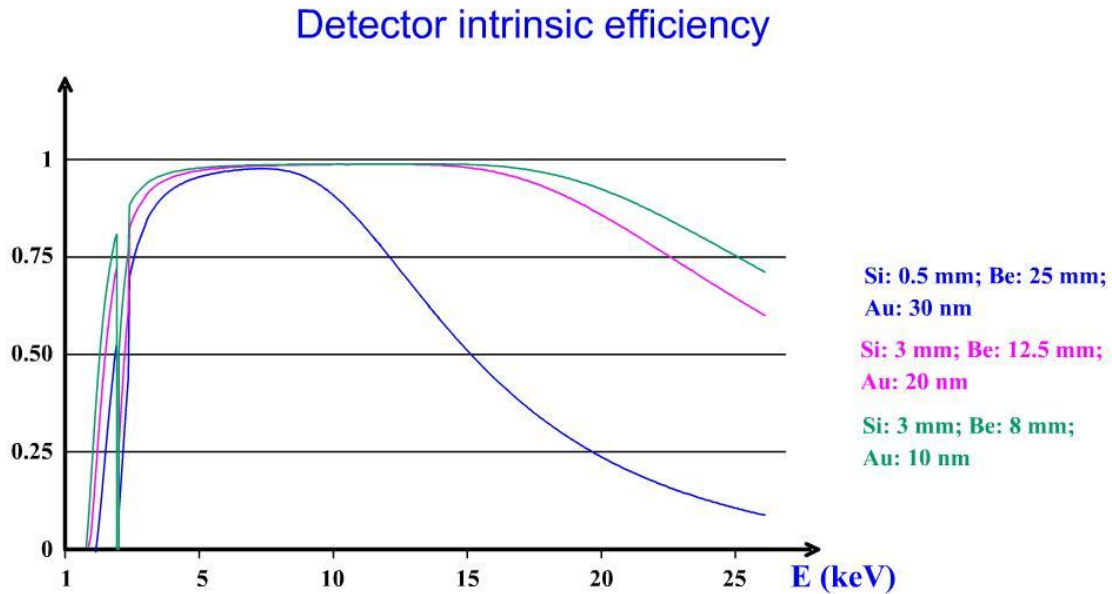
## 2.1.8- Spectrometer energy resolution

The recorded XRF spectra show peaks that span some 10-20 channels, with nearly a Poisson distribution. Such spread is conditioned by the fluctuations in judging the pulse amplitude due to the intrinsic variation in detector response and due to the electronic noise of the system.

Each peak can be characterized by a width defined as the full width at half-maximum (FWHM). This parameter is called spectral resolution.

Conventionally, the resolution is only specified for the Mn- Kα peak (5.9 keV). The resolution is one of the parameters that should be periodically checked, as a criterion of the performance of a particular spectrometer.
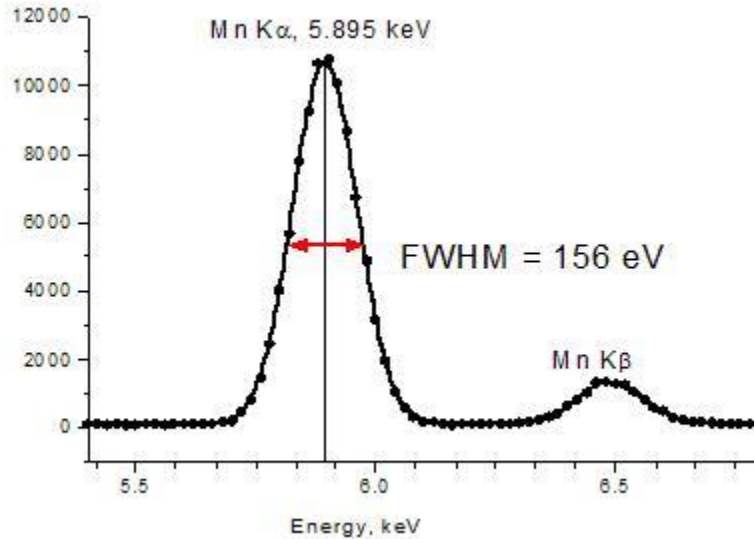
2.1.9- Spectrometer dead time

The number pulses produced by the detector within a certain time interval is called input rate. The number of pulses being processed by the electronic track and indicated by the MCA is defined as the output rate. The input and the output rates differ from one another due to the dead-time of the system.

> The dead time is the period of time during which the system is processing a previous event.

2.2- Excitation sources

Although there are several sources of x-rays, on the laboratory praxis TXRF is performed using X-ray tubes for excitation.

2.2.1- X-ray tube structure

X-ray tubes provide the primary X-rays beam by which the sample is excited to fluorescence. Fine focus X-ray tubes with a fixed anode are generally used for TXRF. An X-ray tube consist of a spiral filament acting as the cathode and a water cooled block of copper as the anode.

Both electrodes are sealed off in an evacuated glass-(ceramic)-metal cylinder.

The filament made out of Tungsten wire is embedded in a narrow steel groove (1 mm x 10 mm).

The copper block is platted with the actual tube anode material. Molybdenum is probably the most widely used anode material for TXRF.
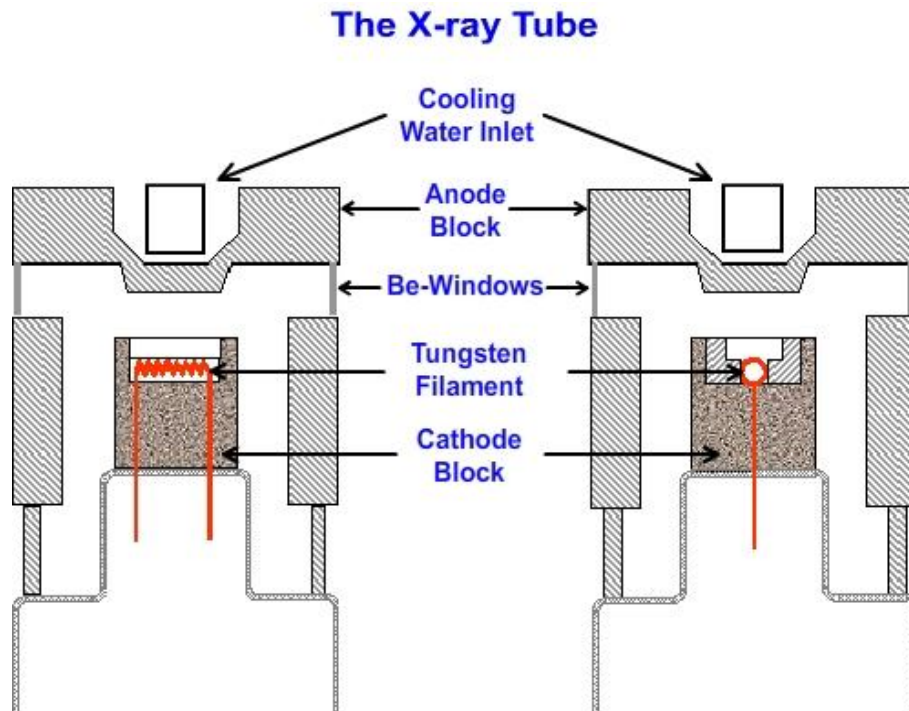
2.2.2- The principle of x-ray tube operation

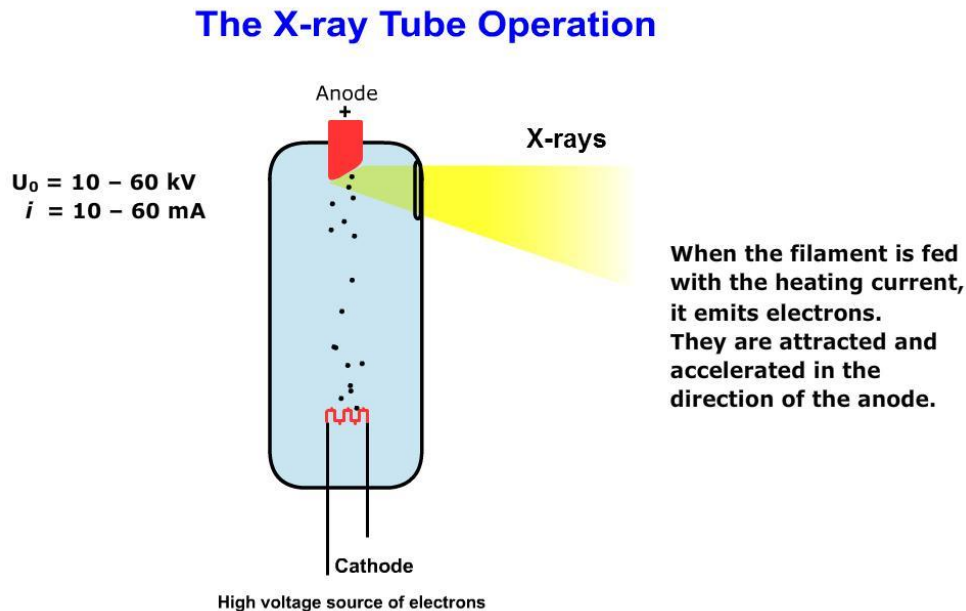When the filament is fed with the heating current, it emits electrons. They are attracted and accelerated in the direction of the anode (~ 20 mm). Since for total reflection condition alignment a good focusing is required, fine focus tube are preferred, for which the bombarded area is ~ 0.25 mm x 10 mm. Fine-focus X-ray tubes are available with several target (anode) materials: Au, W, Ag, Mo, Cu, Co, Fe, Cr, among others.

A proper flux for TXRF excitation can be obtained from x-rays tubes operating at maximal power in the range of 2 – 3 kW. Besides x-ray emission, some energy is released in the form of heat at the anode material, and therefore the x-ray tube must be cooled to avoid its damage. Typically water cooling systems are used for this purpose, with a water consumption of about 4L/min at a pressure of 3-5 bar and a temperature of 20-25°C. The tubes' life can span some 3000-6000 working hours. To ensure a long live operation warm-up conditioning should take between 15 to 45 min, depending on the period of interruption, and the cooling-down time should last for at least 10 min. The nominal value for maximum power of operation should never be exceeded.

The X-rays are emitted in all directions but, out of the tube they emerge only through a side window. The diameter of the window is ~ 6mm and its distance to the bombarded area is ~ 30mm. This means that the beam leaving the tube will be a cone with an aperture of ~ 12°. By tilting the tube by 6°, the beam axis can run horizontally. From the outside the focus of the tube is "observed" under 6° and "looks" like a line of 0.25 mm x 10 mm.

The X-ray Tube Operation

When the filament is fed with the heating current, it emits electrons. They are attracted and accelerated in the direction of the anode.

Anode +

X-rays

$U_0 = 10 - 60$ kV
$i = 10 - 60$ mA

Cathode

High voltage source of electrons

2.2.3- The X-ray Tube spectrum

The distribution of probability of emission by energies (spectrum of the X-ray tube) is ruled by the two effects originating x-ray emission:

- A continuum distribution, characterized by a minimum and a maximum energy which corresponds to the emission of breaking radiation (Bremstrahlung). When operated at voltage U_0 the electrons get a maximal energy $E_0 = e\,U_0$, but photons originated by breaking process can be emitted with energies from E_0 down to zero.

- The characteristic radiation emitted as a result of the ionization of the anode material.

Emission from an X-Ray Tube

$$N(E)\partial E = kiZ\left(\frac{E_0}{E-1}\right)\partial E$$
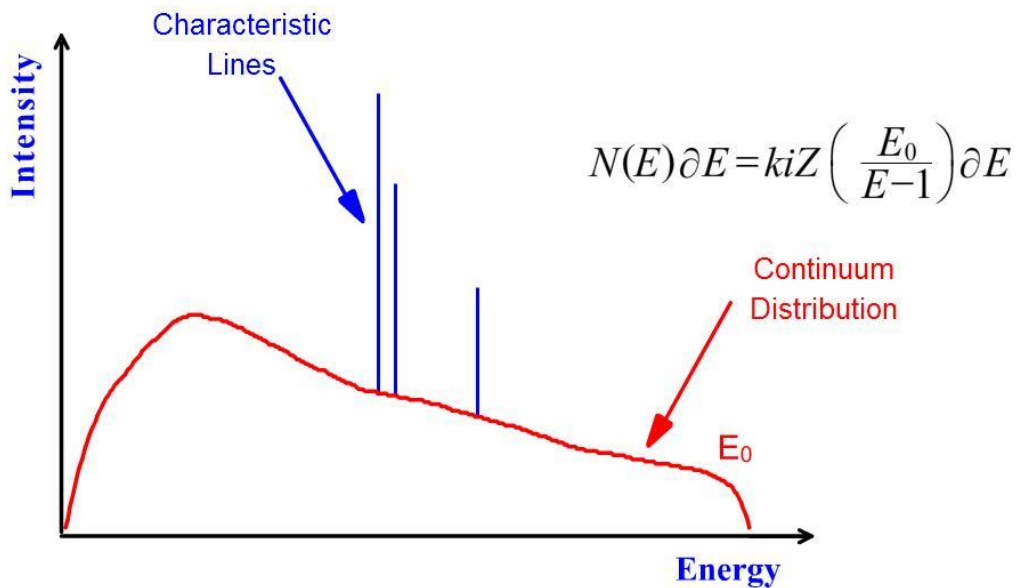
2.3- Modifying the excitation spectrum

Since the intensity of the Bremstrahlung from the x-ray tube is of several orders of magnitudes lower than that of the characteristic emission from the anode most of the x-ray fluorescence production is caused by the latter. Bremstrahlung from the x-ray tube, when scattered at the sample, produces most of the spectrum background on which the x-ray fluorescence peaks are superimposed. Scattered high energy photons not only increase the background in the high energy region of the measured spectra, but also can undertake multiple scatter acts and appear as background in the low energy region as well.

The x-ray tube emission used for excitation can be modified in order to improve the signal to noise ratio in the resulting total reflection x-ray fluorescence spectrum. Some devices can be used to for this purpose: cut-off reflectors or monochromators.

2.3.1- Cutoff effect

As mentioned before the high energy photons can be removed from the primary beam before it reaches the sample by using a first reflector acting as a low-pass or cut-off filter.

Such a filter can be realized by a simple quartz glass block. It represents an ideal low-pass filter if applied as a totally reflecting mirror. At a given angle of incidence, low energy photons are totally reflected whereas high energy photons are absorbed or scattered. This angle is called the cut-off angle.
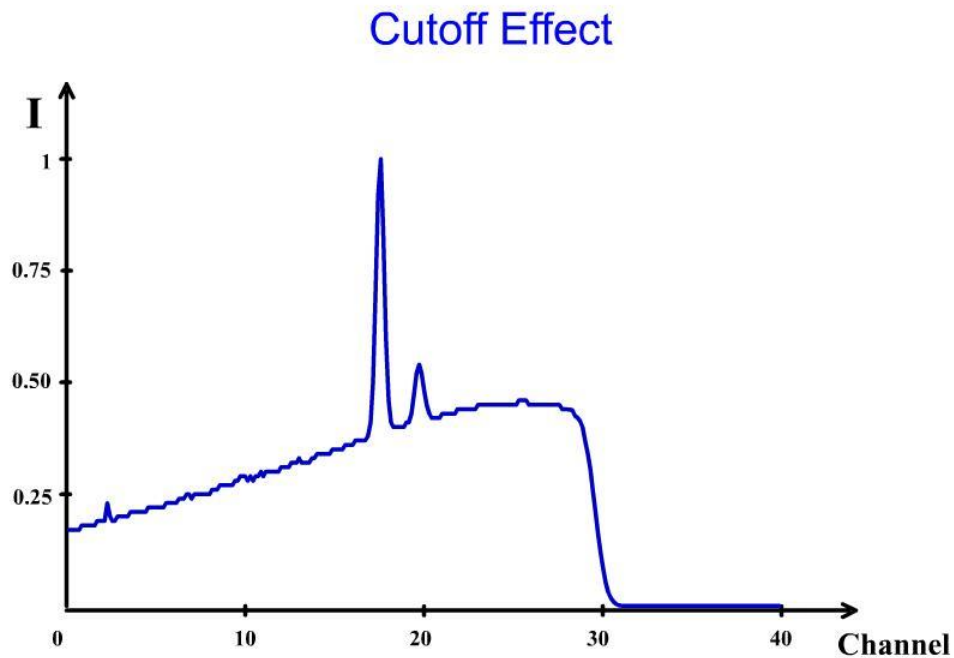
2.3.2- Monochromators

An improvement over cutoff reflectors in terms of lowering the background of the recorded spectra is the use of monochromatic excitation beam. The monochromatization of the X-rays can be realized neither by a low pass filter, not by a foil filter but only by a monochromator: a natural crystal or a synthetic multilayer structure. Both types of monochromators are used as Bragg reflectors, with a definite energy band selected at a particular angle of reflection. This angle should be set in accord to the Bragg's Law **(2dsinθ = nλ)**. For a chosen photon energy E in keV the angle can be calculated by:

$$\alpha = \arcsin\left(\frac{0.620}{E*d}\right)$$

2.3.3- Bragg's Law

From Bragg's Law two important postulates can be asserted:

- A given energy photons are reflected only at certain angle that depends only on the properties of the scattering material.

- A scattering reflector set on a particular angle will reflect only certain photons out of a polychromatic beam. Those, the energy of which fulfills the Bragg' Law.

> It is worth mentioning that the use of a monochromator does not necessarily imply better detection limits. This is particularly true for the low energy zone of the analytical lines.

2.3.4- The mechanism of Bragg's diffraction

When X-rays hit an atom, they make the electronic cloud move as does any electromagnetic wave. The movement of these charges re-radiates waves with the same frequency (blurred slightly due to a variety of effects); this phenomenon is known as the Rayleigh scattering (or elastic scattering). These re-emitted waves interfere with each other either constructively or destructively (overlapping waves either add together to produce stronger peaks or subtract from each other to some degree).

The interference is constructive when the phase shift is a multiple to 2π; this condition can be expressed by Bragg's law: **2dsinθ = nλ**

where:
n is an integer determined by the order given.
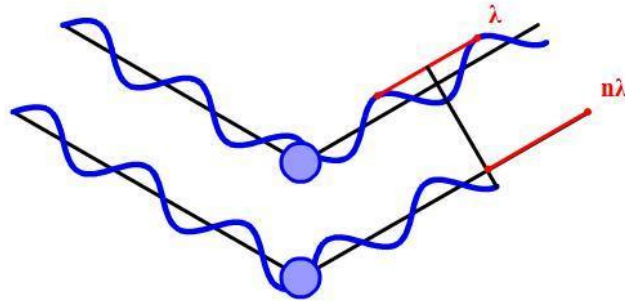**λ** is the wavelength of X-rays.
d is the spacing between the planes in the atomic lattice.
θ is the angle between the incident ray and the scattering planes.

2.3.5- Representation of the Bragg's law

$$\lambda = 6.0$$
$$d = 6.0$$
$$\theta = 30$$

If n is equal to any integer value, the reflected waves will be in phase and constructive interference will occur.
λ: is the wavelength of the incident X-ray beam.
d: is the distance between atomic layers in a crystal.
θ: is the angle of incidence.

$$n\lambda = 2d \sin(\theta)$$
$$n = 2d \sin(\theta) / \lambda$$
$$n = 1.00$$

Constructive interference

2.3.6– Multilayer structured mono-chromators

The use of single crystals for monochromatization of the excitation radiation in TXRF results in relative low efficiency for x-ray fluorescence production. Due to the strict arrangement of the crystalline structure, only small part of the selected x-ray anode characteristic radiation line (e.g. Ka with energies $E_0 \pm \Delta E$) fulfils the condition of Bragg diffraction. In practice, the intensity of the diffracted beam is of about 5 % of the intensity of characteristic radiation in the primary beam.

Multilayered structured devices have been developed on the basis of arranging consecutive layers of a light element and a heavier element on a flat polished reflector, thus creating a periodic (*2D* pseudo-crystalline, with a total thickness of several hundreds of nm) structure ensuring a larger effective reflectivity (~ 30 to 70 %). While adjusting the tilt angle of these devices respective to the incident beam it is possible to observe the occurrence of both total reflection (on the substrate) and Bragg diffraction (on the multilayered structure) effects.

Modification of the Excitation Spectrum
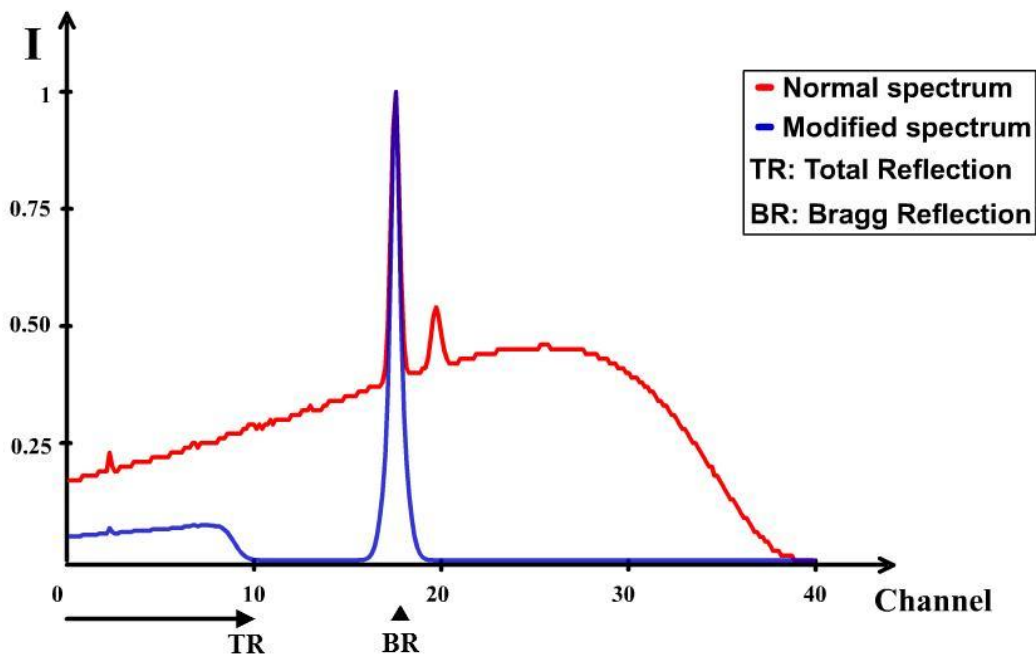
2.4- Sample positioning

For the analysis of trace amounts of elements, a minute amount of sample is deposited in the surface of a flat sample carrier. This sample carrier is positioned in a way that the excitation beam undergoes total reflection on its surface. The advantages of such configuration are an increased instrumental sensitivity and improved detection limits.

The sample is excited by both the incident and the reflected beam, thus increasing the excitation efficiency almost by a factor of two. It is worth to notice that total reflection occurs on the sample carrier surface, but not on the sample itself. On the other hand, the scatter of the excitation radiation towards the detector is minimal at 90 degrees, and it occurs only at the sample (there is no interaction with the sample holder) thus ensuring that the continuum background in the measured spectrum is minimal. These two facts lead to achieve detection limits in the order of ng/g or ng/mL of sample.

2.4.1- Sample carrier

For trace analyses of granular residues, a carrier is required that serves as sample support and as a totally reflecting mirror. They should be highly reflective and optically flat.

The roughness should be less than 5 nm within an area of 1 mm^2, corresponding to about one hundredth of the mean wavelength of the visible light.

The waviness should less than 0.001° within an area of about 1 cm^2, corresponding to a radius of curvature of about 600 m.

Furthermore, carriers should be free of impurities so that no blank values appear for the elements of interest. The carrier material itself must not produce fluorescence peaks in the spectral region to be considered. In addition the carriers have to be chemically inert in relation to strong acids and organic solvents. The carrier should be easy to clean and preferable inexpensive.

Several materials have been used, being fused quartz the most commonly used. The list of other possible materials includes Plexiglas (polymethyl methacrylate), Glassy carbon, boron nitride and synthetic Sapphire, as well as single element materials like Si and Ge.

A small sample is placed in the centre of the reflector

2.5- Adjustment

The process of x-ray optical adjustment of the spectrometer requires of several actions to achieve an optimal characteristic emission to continuum ratio in the measured spectra. Both the excitation spectrum modifier and the sample carrier reflector need to be carefully positioned. The whole process of x-ray optical alignment is aimed to achieving the following four goals:

- Obtaining the more intensive and parallel beam from the x-ray tube.

- Achieving an effective modification of the excitation beam (either by using cut-off effect or a mono-chromator device).

- Removing any remaining part of the x-ray tube beam that might travel over the modifier without interacting with it (direct beam removal).

- Achieving total reflection of the modified excitation beam in the sample carrier reflector.

2.5.1- Primary beam collimation

The radiation emerges from the x-ray tube with some aperture divergence, and the flux intensity varies along the perpendicular to the beam line profile. By placing slit collimators immediately in front of the x-ray tube exit window, one can ensure a high parallelism in the selected line shape beam. If the position and tilt of the collimator can be adjusted (e.g. with some fixing screws) by scanning the beam along the direction perpendicular to the line profile it is possible to select a position corresponding to the maximum flux intensity.

The shape of the collimated beam can be inspected with the help of a ZnS fluorescent screen, and the flux intensity can be assessed if some sample is positioned in the beam line and the radiation scattered at it is measured with the x-ray detector.

2.5.2- The Choice of excitation spectrum modifier

Modification of the excitation spectrum is required to remove from it the Bremstrahlung-origin photons, which will contribute to increased continuum background under the fluorescence peaks in the measured spectrum due to scatter at the sample residue. There are two main phenomena that can be used to achieve this goal:

- Using total-reflection of the primary beam at some polished sample (cut-off reflector). The tilt angle of the cut-off reflector is selected as to ensure the total reflection condition for photons with energy up to those of the main characteristic emission photons from the x-ray tube anode (Ka and Kb). If one chooses a tilt angle corresponding to the critical angle for anode Kb energy, the higher energies will be refracted in the reflector and removed from the totally reflected beam. The advantage of using Total reflection is that of having not only the largest possible intensity flux (anode Ka + Kb), but also the capability of exciting better the elements with low atomic number with the lower energies continuum component. This solution is particularly suitable for the analysis of solutions containing low amounts of dissolved salts, such as high purity acids or injection degree quality water. In such case the detection limits will be not so heavily affected, since the background in the measured spectrum due to scatter of the continuum in the residues will be not so appreciable.

- Using Bragg diffraction at a multi-layered structure device, tilted under an angle that will correspond to the diffraction of the anode Ka photons. In such case, the diffracted beam is of a high mono-chromaticity, a feature that is particularly useful for the analysis of samples with large residues. Although the x-ray production is less than in the case of using a cut-off reflector, the detection limits can be significantly improved due to the decrease of the continuum background.

2.5.3- X-ray optics adjustment

The process of adjustment of either the spectrum modifier or the sample carrier reflector (further on referred to as 'device') is based on the same procedure. The device shall be mounted in a plate holder that could be tilted as to reach a parallel plane and later on to adjust its tilt in regard to the beam line. Three screws in combination with springs can be used for this purpose. The interaction of the beam with the device can be monitored by observing the resulting shape of the beam and the appearance of the diffracted/reflected beam and their shape using a ZnS fluorescent screen (in a darkened room) or a CCD camera (see figure).
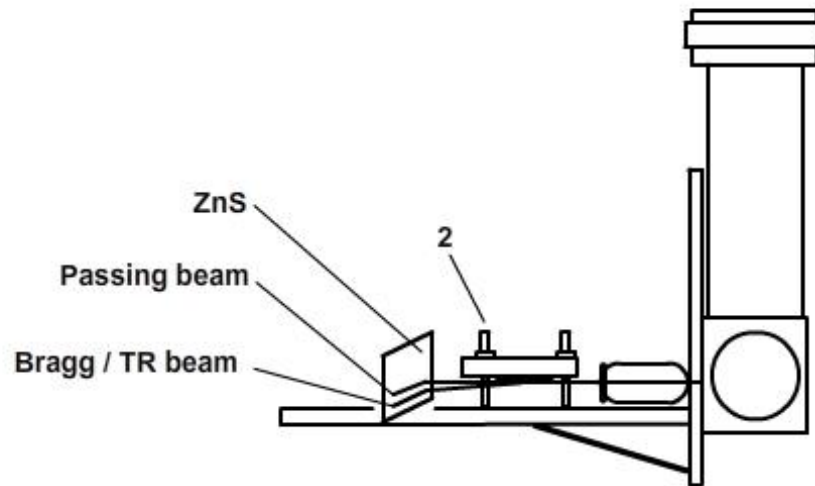
2.5.4- Illustration of TR condition adjustment

The adjustment of the reflector plate is changed by moving the three adjustment screws. The effect of the positioning the reflector plate can be assessed by observing the shape of the beam (either by observing its fluorescence in a ZnS screen in the dark or in a CCD camera).