

Introduction to X-ray Fluorescence Analysis (XRF)

- Fundamental Principles, Instrumentation

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Fundamental Principles

Electromagnetic Radiation, Photons

From a physical point of view, X-rays are of the same nature as visible light. Visible light can be described as electromagnetic wave radiation whose variety of colors (e.g. the colors of the rainbow) we interpret as different wavelengths. The wavelengths of electromagnetic radiation reach from the kilometer range of radio waves up to the picometer range (10^{-12} m) of hard gamma radiation (Tab. 1).

Tab. 1: Energy and wavelength ranges of electromagnetic radiation.

Energy range (keV)	Wavelength range	Name
< 10 ⁻⁷	cm to km	Radio waves (short, medium, long waves)
< 10 ⁻³	μm to cm	Microwaves
< 10 ⁻³	μm to mm	Infrared
0.0017 – 0.0033	380 to 750 nm	Visible light
0.0033 – 0.1	10 to 380 nm	Ultraviolet
0.11 – 100	0.01 to 12 nm	X-rays
10 – 5000	0.0002 to 0.12 nm	Gamma radiation

In the following text, the unit nanometer (nm = 10^{-9} m) is used for the wavelength, λ (= Lambda), and the unit kiloelectronvolts (keV) for energy, E.

Comment

In literature the unit Angström (Å) is often stated for the wavelength:

$$1 \text{ \AA} = 0.1 \text{ nm} = 10^{-10} \text{ m}$$

The following relationship (conversion formula) exists between the units E (keV) and λ (nm):

$$E(\text{keV}) = \frac{1.24}{\lambda(\text{nm})} \text{ or } \lambda(\text{nm}) = \frac{1.24}{E(\text{keV})}$$

The X-ray fluorescence analysis records the following range of energy or wavelengths:

$$E = 0.11 - 60 \text{ keV}$$

$$\lambda = 11.3 - 0.02 \text{ nm}$$

Apart from the wave properties, light also has the properties of particles. This is expressed by the term "photon". In the following we will be using the term **photons** or **X-ray photons** for this.

The radiation **intensity** is the number of X-ray photons that are emitted or measured per unit of time. We use the number of X-ray photons measured per second, cps (= counts per second) or **kCps** (= kilocounts per second) as the unit of intensity.

The Origin of X-rays

Electromagnetic radiation can occur whenever electrically charged particles, particularly electrons, lose energy as a result of a change in their state of motion, e.g., upon deceleration, changing direction or moving to a lower energy level in the atomic shell. The deceleration of electrons and the transition from an energy level in the atomic shell to a lower one play an important part in the creation of X-rays in the field of X-ray analysis. To understand the processes in the atomic shell we must take a look at the Bohr's atomic model.

Bohr's Atomic Model

Bohr's atomic model describes the structure of an atom as an atomic nucleus surrounded by electron shells (Fig. 1):

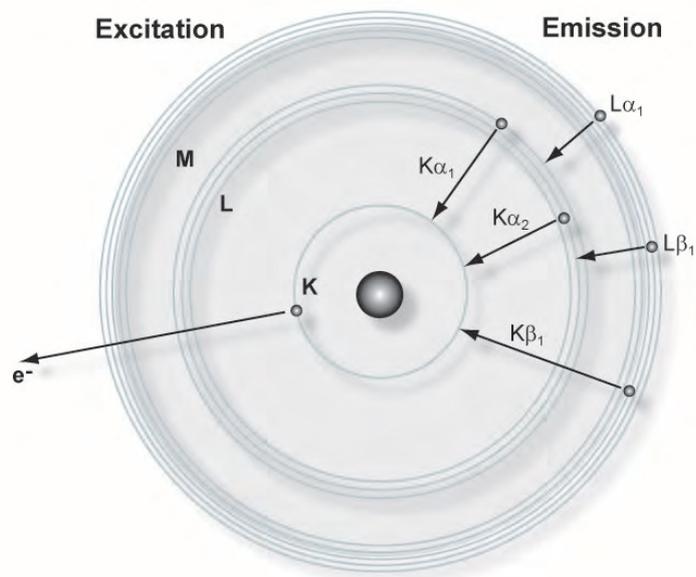


Fig. 1: Bohr's atomic model, shell model.

The positively charged nucleus is surrounded by electrons that move within defined areas ("shells"). The differences in the strength of the electrons' bonds to the atomic nucleus are very clear depending on the area or level they occupy, i.e. they vary in their energy. When we talk about this we refer to energy levels or energy shells. This means: A clearly defined minimum amount of energy is required to release an electron of the innermost shell from the atom. To release an electron of the second innermost shell from the atom, a clearly defined minimum amount of energy is required that is lower than that needed to release an innermost electron. An electron's bond to an atom is weaker the further away it is from the atom's nucleus. The minimum amount of energy required releasing an electron from the atom, and thus the energy with which it is bound to the atom, is also referred to as the **binding energy** of the electron to the atom.

The binding energy of an electron in an atom is established mainly by determining the incident. It is for this reason that the term **absorption edge** is very often found in literature:

Energy level = binding energy = absorption edge

The individual shells are labeled with the letters **K, L, M, N**; the innermost shell being the **K-shell**, the second innermost the **L-shell** etc. The K-shell is occupied by 2 electrons. The L-shell has three sub-levels and can contain up to a total of 8 electrons. The M-shell has five sub-levels and can contain up to 18 electrons.

Characteristic Radiation

Every element is clearly defined by its atomic number Z in the periodic system of elements or by the number of its electrons in a neutral state. The binding energies or the energy levels in every element are different and characteristic for every element as a result of the varying number of electrons (negative charges) or the number Z of the positive charges in the atomic nucleus (= atomic number).

If an electron of an inner shell is now separated from the atom by the irradiation of energy, an electron from a higher shell falls into this resultant "hole" which releases an amount of energy equivalent to the difference between the energy levels involved.

The energy being released can be either be emitted in the form of an X-ray or be transferred to another atomic shell electron (Auger effect). The probability of an X-ray resulting from this process is

called the **fluorescence yield ω** . This depends on the element's atomic number and the shell in which the "hole" occurred. ω is very low for light elements (approx. 10^{-4} for boron) and almost reaches a value of 1 for the K-shell of heavier elements (e.g. uranium).

However, decisive is that the energy or wavelength of the X-ray is very characteristic for the element from which it is emitted; such radiation is called **characteristic X-rays**.

This provides the basis for determining chemical elements with the aid of **X-ray fluorescence analysis**.

Nomenclature

The energy of an X-ray corresponds to the difference in energy of the energy levels concerned. K-radiation is the term given to the radiation released when replenishing the K-shell, L-radiation to that released when replenishing the L-shell etc. (Fig. 2).

Also needed for the full labeling of the emitted X-ray line is the information telling us which shell the electron filling the "hole" comes from. The Greek letters α , β , γ , ... are used for this with the numbering 1, 2, 3, ... to differentiate between the various shells and sub-levels.

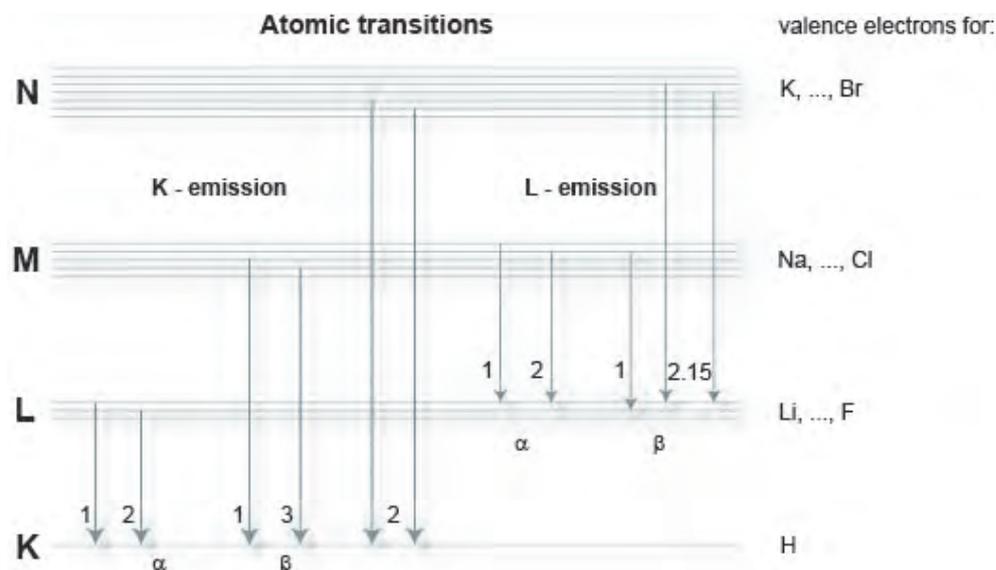


Fig. 2: X-ray line labeling.

Examples:

- $K\alpha_1$ Electron from sub-level L_{III} to the K-shell ($K\alpha_1$)
- $K\alpha_2$ Electron from sublevel L_{II} to the K-shell ($K\alpha_2$)
- $K\alpha_{1,2}$ if neither line is resolved by the spectrometer: $K\alpha_{1,2}$
- $K\beta_1$ Electron from sublevel M to the K-shell ($K\beta_1$)
- $L\alpha_1$ Electron from sublevel M to the L-shell ($L\alpha_1$)

Generating the Characteristic Radiation

The purpose of X-ray fluorescence is to determine chemical elements both qualitatively and quantitatively by measuring their characteristic radiation. To do this, the chemical elements in a sample must be caused emit X-rays. As characteristic X-rays only arise in the transition of atomic shell electrons to lower, vacant energy levels of the atom, a method must be applied that is suitable for releasing electrons from the innermost shell of an atom. This involves adding to the inner electrons amounts of energy that are higher than the energy bonding them to the atom.

This can be done in a number ways:

- Irradiation using elementary particles of sufficient energy (electrons, protons, α -particles, ...) that transfer the energy necessary for release to the atomic shell electrons during collision processes
- Irradiation using x- or gamma rays from radionuclides
- Irradiation using X-rays from an **X-ray tube**

Using an X-ray tube here proves to be the technically most straightforward and, from the point of view of radiation protection, the safest solution (an X-ray tube can be switched off, a radionuclide cannot).

X-ray Tubes, Bremsspektrum

In an X-ray tube, electrons are accelerated in an electrical field and shot against a target material where they are decelerated. The technical means of achieving this is to apply high voltage between a heated cathode (e.g. a filament) and a suitable anode material. Electrons emanate from the heated cathode material and are accelerated towards the anode by the applied high voltage. There they strike the anode material and lose their energy through deceleration. Only a small proportion of their energy loss (approx. 1-2 %, depending on the anode material) is radiated in the form of X-rays. The greatest amount of energy contributes to heating up the anode material. Consequently the anode has to be cooled which is achieved by connection to a water-cooling system.

The proportion of the electron energy loss emitted in the form of an X-ray can be between zero and the maximum energy that the electron has acquired as a result of the acceleration in the electrical field. If 30 kV are applied between the anode and cathode, the electrons acquire 30 keV from passing through this voltage (kiloelectron volts) (Definition: 1 eV = the energy that an electron acquires when passing through a potential of 1 Volt).

A maximum X-ray energy of 30 keV can be acquired from deceleration in the anode material, i.e. the distribution of the energies of numerous X-rays is between zero and the maximum energy. If the intensity of this type of X-ray is applied depending on the energy, the result is the **Bremsspektrum** (= continuum) of the tube.

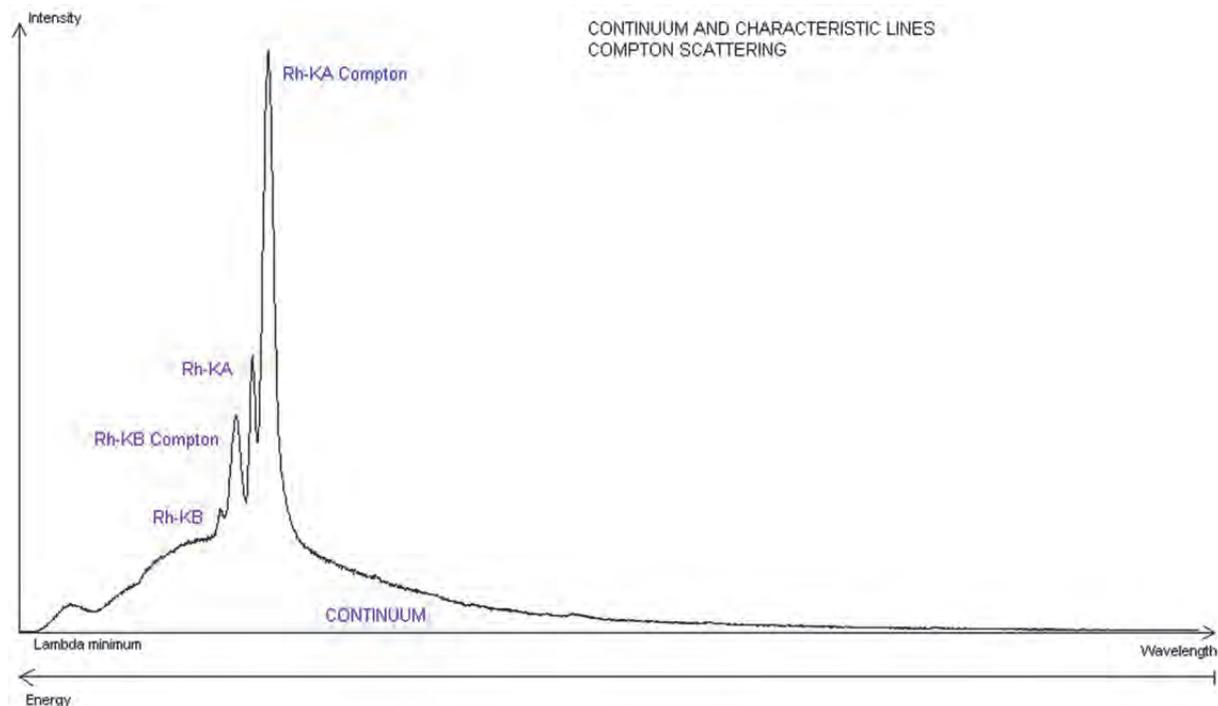


Fig. 3: A Bremsspektrum (= continuum) with characteristic radiation of the anode material.

In addition to the Bremspektrum, an X-ray tube of course emits the characteristic radiation of the anode material as well which is of major importance for the X-ray fluorescence analysis (Fig. 3).

Tube Types, Generator

All X-ray tubes work on the same principle: accelerating electrons in an electrical field and decelerating them in a suitable anode material. The region of the electron beam in which this takes place must be evacuated in order to prevent collisions with gas molecules. Hence there is a vacuum within the housing. The X-rays escape from the housing at a special point that is particularly transparent with a thin beryllium window.

The main differences between tube types are in the polarity of the anode and cathode and the arrangement of the exit window. The two most significant types are the end-window tubes and the side-window tubes. The side-window tube design is the historical design, whereas today for modern XRF- instruments only end-window tubes are used due to the higher efficiency.

Side-window Tubes

In the past side window tubes were used for XRF instrumentation. In side-window tubes, a negative high voltage is applied to the cathode. The electrons emanate from the heated cathode and are accelerated in the direction of the anode. The anode is set on zero voltage and thus has no difference in potential to the surrounding housing material and the **laterally** mounted beryllium exit window (Fig. 4).

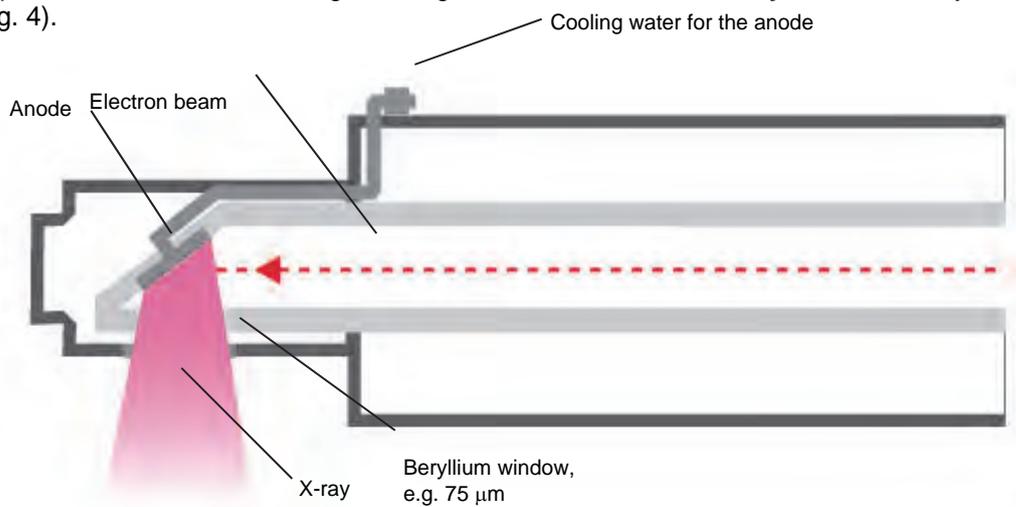


Fig. 4: The principle of the side-window tube.

For physical reasons, a proportion of the electrons are always scattered on the surface of the anode. The extent to which these **back-scattering electrons** arise depends, amongst other factors, on the anode material and can be as much as 40 %. In the side-window tube, these back-scattering electrons contribute to the heating up of the surrounding material, especially the exit window. As a consequence, the exit window must withstand high levels of thermal stress any cannot be selected with just any thickness. The minimum usable thickness of a beryllium window for side-window tubes is 300 μm. This causes an excessively high absorption of the low-energy characteristic L radiation of the anode material in the exit window and thus a restriction of the excitation of lighter elements in a sample.

End-window Tubes

Modern XRF instrumentation is using due to the better efficiency means higher primary intensity end-window X-ray tubes. The distinguishing feature of the end-window tubes is that the anode has a **positive** high voltage and the beryllium exit window is located on the **front end** of the housing (Fig. 5).

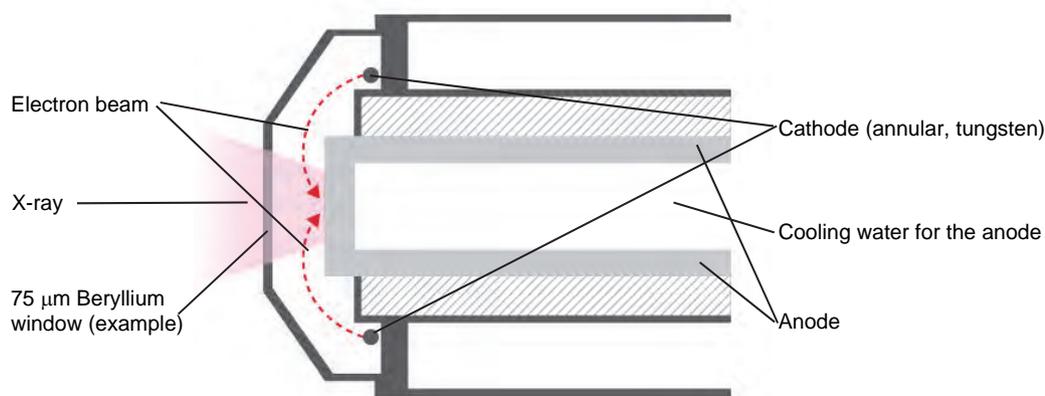


Fig. 5: The principle of the end-window tube.

The cathode is set around the anode in a ring (angular cathode) and is set at zero voltage. The electrons emanate from the heated cathode and are accelerated towards the electrical field lines on the anode. Due to the fact that there is a difference in potential between the positively charged anode and the surrounding material, including the beryllium window, the back-scattering electrons are guided back to the anode and thus do not contribute to the rise in the exit window's temperature. The beryllium window remains "cold" and can therefore be thinner than in the side-window tube. Windows are typically used with a thickness of 75 µm, older design will have thicknesses of about 125 µm. Actually the tube window thicknesses become thinner to 50 µm. This provides a prerequisite for exciting light elements with the characteristic L radiation of the anode material (e.g. rhodium).

Due to the high voltage applied, non-conductive, de-ionized water must be used for cooling. Instruments with end-window tubes are therefore equipped with a closed, internal circulation system containing de-ionized water that cools the tube head as well.

End-window tubes have been implemented by all renowned manufacturers of wavelength dispersive X-ray fluorescence spectrometers since the early 80's.

Generator

The current, the high voltage for the X-ray tubes and the heating current for the cathode are produced in the X-ray generator. The generators available today supply a maximum tube current of 150 mA and a maximum high voltage of 60 kV at a maximum output of 4 kW, i.e. current and voltage must be selected in such a way that 4 kW is not exceeded. The architecture of modern control electronics and software ensures that damage to the tube resulting from maladjustment is impossible. The reason for restricting the maximum excitation power to 1 kW is that cooling with external coolant can be dispensed with which simplifies installation requirements.

Excitation of Characteristic Radiation in Sample Material

The Bremsstrahlung and the characteristic radiation of the X-ray tube's anode material are used to excite the **characteristic radiation of the elements in the sample material**. It is very important to know that a chemical element in the sample can only be made to emit X-rays when the energy of the incident X-ray photons is higher than the binding energy (absorption edge) of the element's inner electrons. If the sample is irradiated with a tube high-voltage of e.g. 20 kV, the maximum energy of the photons emitted from the tube is 20 keV. Hence, it is impossible, for example, to excite the K radiation of the elements that have an atomic number $Z \geq 43$ as their K binding energy is greater than 20 keV. Excitation of the K radiation of heavier elements is achieved with a generator setting of 60 kV.

All renowned manufacturers use rhodium (Rh) as the standard anode material as the characteristic energies of this element are simultaneously suitable for exciting both heavy and light elements.

Energies and wavelengths of rhodium's characteristic lines, and the heaviest element that can be excited with the appropriate line in each case, are listed in Tab. 2.

Tab. 2: Rhodium's characteristic lines.

Line	Energy	Wavelength	Heaviest element
Rh Ka1	20.214 keV	0.0613 nm	Molybdenum (Mo)
Rh Ka2	20.072 keV	0.0617 nm	Molybdenum (Mo)
Rh Ka1	22.721 keV	0.0546 nm	Ruthenium (Ru)
Rh La1,2	2.694 keV	0.4601 nm	Sulphur (S)
Rh La1	2.834 keV	0.4374 nm	Chlorine (Cl)

The following can be extracted from Tab. 2:

- The K lines of the heavy elements from rhodium to tantalum (Ta) can, on principle, only be excited with the **Bremsstrahlung** of the rhodium tube as the energy of the rhodium lines is insufficient to do it. A generator setting of 60 kV is recommended for such cases.
- The elements as far as molybdenum are excited by the Rh K radiation. The Rh-K β_1 radiation can even excite the element ruthenium but is of lower intensity than the K-alpha radiation.
- The light elements up to sulphur are excited very effectively by the Rh L radiation.
- The Rh-L β_1 radiation can excite the element chlorine but is of a lower intensity. Decisive for the available intensity of the Rh L radiation is the thickness of the tube's **beryllium exit window**.

Instead of rhodium, other elements can be used as an anode material for special applications. Tungsten (W) and gold (Au) are particularly suitable for exciting heavier elements with the Bremspektrum. Chromium (Cr) was often used in side-window tubes for exciting lighter elements. Molybdenum (Mo) was frequently used for the interference-free measurement of rhodium and, for example, cadmium.

The use of the rhodium end-window tube as a "universal tube" is justified as the light elements can be excited far more effectively with the Rh L radiation than with the K radiation of a chromium anode. Moreover, instrument technology is so advanced nowadays that measuring rhodium itself (or cadmium) presents no problem. Please also refer to the technique of the primary beam filter, page 30.

Absorption, the Mass Attenuation Coefficient

Passing through matter weakens the intensity of X-rays. The degree of this weakening depends on both the radiation energy and the chemical composition of the absorbing material (e.g. the sample). Heavier elements absorb better than light ones: 1 mm of lead absorbs practically all of the higher-energy radiation occurring during X-ray fluorescence; 1 mm of polypropylene (hydrocarbon) is more or less permeable to X-rays. Low-energy X-ray photons are absorbed more readily than photons with higher energy (= short wavelengths): the photons emitted by the element boron, for example, have a very low energy of 0.185 keV (= 67 nm) and are practically completely absorbed by even 6 μm of polypropylene foil.

If an X-ray with photons of energy E and an intensity of I_0 pass through a layer of material, e.g., 1 mm sheet of pure iron (Fe), the ray emerging from behind the iron layer will only be left with the intensity $I < I_0$ as a result of the absorption. The relationship between I and I_0 after the transition through the layer thickness x is described by the law of absorption:

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

μ = linear absorption coefficient

The linear absorption coefficient has the dimension [1/cm] and is dependent on the energy or the wavelength of the X-ray photons and the special density ρ (in [g/cm³]) of the material that was passed through.

If the iron sheet in the above example is replaced by a 1 mm layer of iron powder, the absorption is less because the density of the absorber is lower. Therefore, it is not the linear absorption coefficient that is specific to the absorptive properties of the element iron, but the coefficient applicable to the density ρ of the material that was passed through

$$\mu / \rho \quad = \text{mass attenuation coefficient}$$

The mass attenuation coefficient has the dimension [cm^2/g] and only depends on the atomic number of the absorber element and the energy, or wavelength, of the X-ray photons.

Fig. 6 illustrates the schematic progression of the mass attenuation coefficients depending on the energy or wavelength.

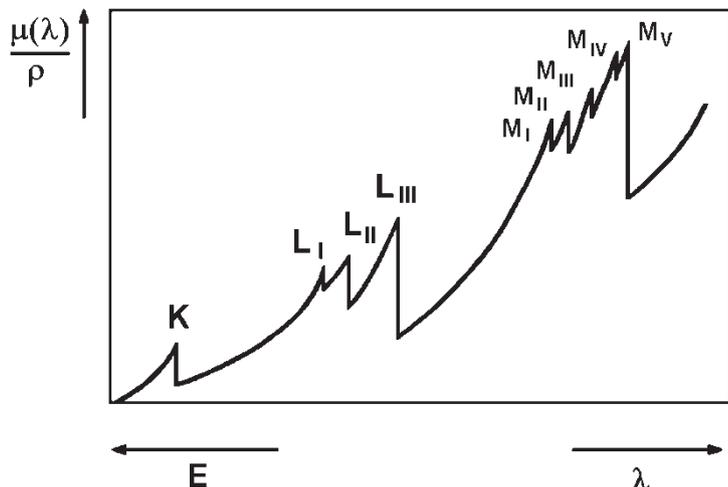


Fig. 6: Schematic progression of the mass attenuation coefficient of energy or wavelength.

Fig. 6 supplies the following:

- The overall progression of the coefficient decreases as energy increases, i.e. the higher the energy of the X-ray photons, the less they are absorbed.
- The rapid changes in the mass attenuation coefficient reveal the binding energies of the electrons in the appropriate shells. If an X-ray photon has a level of energy that is equivalent to the binding energy of an atomic shell electron in an appropriate shell, it is then able to transfer all its energy to this electron and displace it from the atom. In this case, absorption increases sharply. Photons whose energy is only slightly below the absorption edge are absorbed far less readily.

Example:

The K radiation of iron (Fe) is absorbed less by its neighboring element manganese (Mn) than by the element chromium (Cr) as Fe $K\alpha_{1,2}$ is below the absorption edge of Mn but above that of Cr.

Layer Thickness, Saturation Thickness

The more readily the radiation of an element in the sample material is absorbed, the smaller is the layer of the sample from which the measurable radiation comes. A K-alpha photon from the element molybdenum (Mo $K\alpha_1$, 17.5 keV) has a far greater chance of being measured at a depth of 0.5 mm from the analysis surface of a steel sample than a photon from carbon (C $K\alpha_{1,2}$, 0.282 keV). As a consequence, a specific layer thickness is analyzed for each element which depends on the specific energy of the used element line. The analysis of very light elements e.g. in solids (such as Be, B, C ..., for example) is comparable with a plain surface analysis as their radiation originates from few atomic layers. Practically all the radiation from deeper layers is fully absorbed within the sample.

A sample is referred to as being **infinitely thick** for a radiation component if it is sufficiently thick to practically completely absorb the radiation from the rear. Thus, a 1mm thick sample of cement is practically infinitely thick for Fe $K\alpha_{1,2}$ radiation as the radiation from the rear of the sample is almost fully absorbed in the sample material. The thickness of a sample that is sufficient to absorb the radiation of an element line to a high degree (e.g. 90 %) is called the **saturation thickness**.

Caution is advised with sample materials that are composed of light elements such as liquids or plastics (hydrocarbons). Here, for the high-energy radiation of heavier elements, high saturation

thicknesses that cannot be used in practice (e.g. 10 cm) are easily attainable. Hence, where these material groups are concerned, it must be ensured that identical sample quantities are used for quantitative analysis as the measured intensity may depend on the thickness of the sample.

Applying liquid sample materials to **filter paper** is a method of almost completely preventing the effects of absorption. The term for this is **infinitely thin** samples.

Nowadays, the calculation of those layer thicknesses in defined samples that contribute to the analysis is integrated into modern software packages.

Secondary Enhancement

Secondary enhancement, i.e. those X-ray photons that are produced as a result of the effect of the sample elements' absorbed radiation, is closely linked to produced X-rays' absorption in the sample.

Example:

A Si $K\alpha_1$ photon is produced in a sample by the effect of an X-ray tube's radiation. Inside the sample, it can be absorbed again by transferring its energy to an Al K electron. This can then emit an X-ray photon itself. The silicon radiation thus contributes to the X-ray emission of the aluminum. This is referred to as **secondary enhancement** (Fig. 7).

In quantitative analyses, the effects of absorption and secondary enhancement may have to be corrected. Modern software packages offer a selection of correction models (matrix correction or inter-element correction) for this purpose.

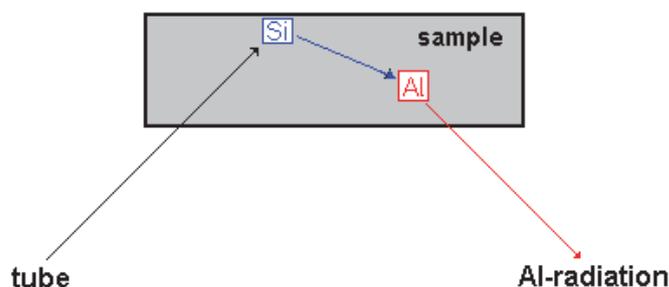


Fig. 7: Secondary enhancement.

Tube-Spectrum Scattering at the Sample Material

The purpose of X-ray fluorescence spectrometry is the qualitative and quantitative determination of the elements in a sample by measuring their characteristic radiation. As the sample is exposed to a beam of X-ray photons from a tube, a proportion of these X-rays also reach the detector in the form of radiation **background** as a result of physical scattering processes. While the scattered Bremsstrahlung proportion generally produces a continuous background, the scattered characteristic radiation of the anode material contributes towards the **line spectrum**. Besides the lines of elements from the sample, the anode material's lines and the scattered Bremspektrum usually appear as well as a background.

The intensity of the scattering depends on the composition of the sample: for samples who are mainly composed of **light elements** (light matrix), the proportion of scattered radiation is **high**. Where samples are concerned that comprise mainly **heavy elements** (heavy matrix), the scattered proportion is relatively **low**.

Background and characteristic scattering can be very effectively reduced by inserting a suitable absorption material between tube and sample.

There are two types of scattering whose physical scattering processes differ from each other and are referred to in literature as follows:

Rayleigh scattering = elastic scattering = classic scattering

Compton scattering = inelastic scattering

We will use the bold terms from now on and elaborate upon the effects of scattered characteristic radiation of the anode material.

Rayleigh Scattering

The Rh photons coming from the tube change their direction in the sample material without losing energy and can thus enter the detector and can be measured. The peaks of the anode material (e.g. rhodium) appear in the line spectrum. If the element rhodium in the sample material is to be analyzed using an Rh tube then the characteristic radiation coming from the tube must be absorbed by a primary beam filter before it reaches the sample (cf. Fig. 25, 29).

Compton Scattering

The Rh photons coming from the tube strike the sample elements' electrons. In this process, some a photon's energy is transferred to an electron. The X-ray photon therefore loses energy. The intensity of the photons scattered by the Compton Effect depends, amongst other factors, on the tube radiation's angle of incidence to the sample and on the take-off angle of the radiation in the spectrometer. As these angle settings are fixed in a spectrometer (cf. beam path), a somewhat wider peak appears on the low-energy side of the appropriate Rh peak. These peaks are called "**Compton peaks**" (cf. Fig. 25, 29).

Measuring X-rays

Detectors, Pulse Height Spectrum

When measuring X-rays, use is made of their ability to **ionize** atoms and molecules, i.e. to displace electrons from their bonds by energy transference. In suitable detector materials, **pulses** whose strengths are proportional to the energy of the respective X-ray photons are produced by the effect of X-rays. The information about the X-ray photons' energy is contained in the registration of the pulse height. The number of X-ray photons per unit of time, e.g. pulses per second (cps = counts per second, kCps = kilocounts per second), is called their **intensity** and contains in a first approximation the information about the concentration of the emitting elements in the sample. Two main types of detectors are used in wavelength dispersive X-ray fluorescence spectrometers: the **gas proportional counter** and the **scintillation counter**.

The detector working principle is described in the following chapters.

Gas Proportional Counter

The gas proportional counter comprises a cylindrical metallic tube in the middle of which a thin wire (**counting wire**) is mounted. This tube is filled with a suitable gas (e.g. Ar + 10 % CH₄). A positive high voltage (+U) is applied the wire. The tube has a lateral aperture or **window** that is sealed with a material permeable to X-ray photons (Fig. 8).

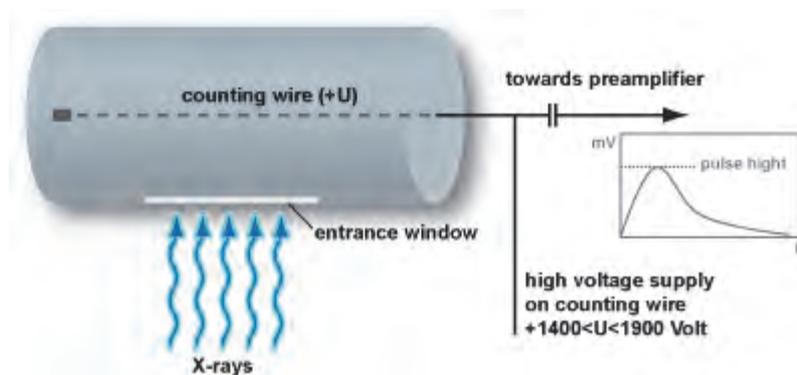


Fig. 8: A gas proportional counter.

An X-ray photon penetrates the window into the counter's gas chamber where it is absorbed by ionizing the gas atoms and molecules. The resultant positive ions move to the cathode (tube), the free electrons to the anode, the wire. The number of electron-ion pairs created is proportional to the energy of the X-ray photon. To produce an electron-ion pair, approx. 0.03 keV are necessary, i.e. the radiation of the element boron (0.185 keV) produces approx. 6 pairs and the K-alpha radiation of molybdenum (17.5 keV) produces approx. 583 pairs. Due to the cylinder-geometric arrangement, the primary electrons created in this way "see" an **increasing** electrical field on route to the wire. The high voltage in the counting tube is now set so high that the electrons can obtain enough energy from the electrical field in the vicinity of the wire to ionize additional gas particles. An individual electron can thus create up to 10.000 secondary electron-ion pairs.

The secondary ions moving towards the cathode produce a measurable signal. Without this process of **gas amplification**, signals from boron, for example, with 6 or molybdenum with 583 pairs of charges would not be able to be measured as they would not be sufficiently discernible from the electronic "noise". Gas amplification is adjustable via high voltage in the counting tube and is set higher for measuring boron than for measuring molybdenum. The subsequent pulse electronics supply pulses of voltage whose height depends, amongst other factors, on the energy of the X-ray photons.

There are two models of gas proportional counters: the **flow counter** ("FC") and the sealed **proportional counter** ("PC"). The flow counter is connected to a continuous supply of counting gas (Ar + 10 % CH₄) and has the advantage of being able to be equipped with a very thin window ($\leq 0.6 \mu\text{m}$). The FC is therefore also suitable for measuring the very light elements and is very stable. The proportional counter, on the other hand, has a closed volume and requires a thick window normally made of beryllium. The absorption in this "thick" beryllium window prevented the measurement of the very light elements (Be to Na).

Since innovative, highly transparent organic materials have been in use, there has now been success in developing sealed proportional counters that are just as sensitive to the very light elements (Be to Na) as flow counters are.

Scintillation Counters

The scintillation counter, "SC", used in XRF comprises a sodium iodide crystal in which thallium atoms are homogeneously distributed 'NaI(Tl)'. The density of the crystal is sufficiently high to absorb all the XRF high-energy photons. The energy of the pervading X-ray photons is transferred step by step to the crystal atoms that then radiate light and cumulatively produce a flash. The amount of light in this scintillation flash is proportional to the energy that the X-ray photon has passed to the crystal. The resulting light strikes a photocathode from which electrons can be detached very easily. These electrons are accelerated in a photomultiplier and, within an arrangement of dynodes, produce so-called secondary electrons giving a measurable signal once they have become a veritable "avalanche" (Fig. 9). The height of the pulse of voltage produced is, as in the case of the gas proportional counter, proportional to the energy of the detected X-ray photon.

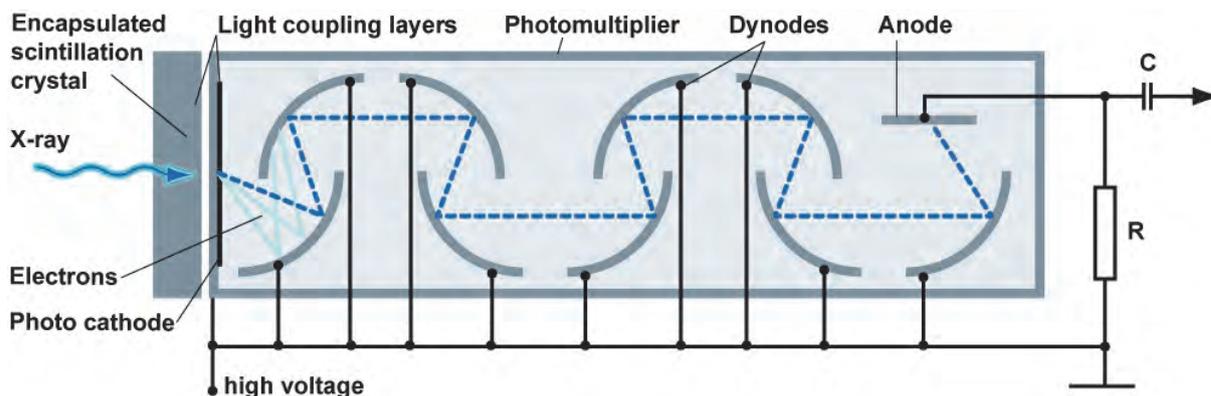


Fig. 9: Scintillation counter including photomultiplier.

Pulse Height Analysis (PHA), Pulse Height Distribution

If the **number** of the measured pulses (intensity), which are dependent on the pulse height, are displayed in a graph, we have the “pulse height spectrum”. Synonymous terms are: “pulse height analysis or “pulse height distribution”. As the height of the pulses of voltage is proportional to the X-ray photons’ energy, it is also referred to as the **energy spectrum** of the counter (Fig. 10). The pulse height is given in volts, scale divisions or in “%” (and could be stated in keV after appropriate calibration). The “%”-scale is defined in such a way (SPECTRA^{plus}) that the peak to be analyzed appears at 100 %.

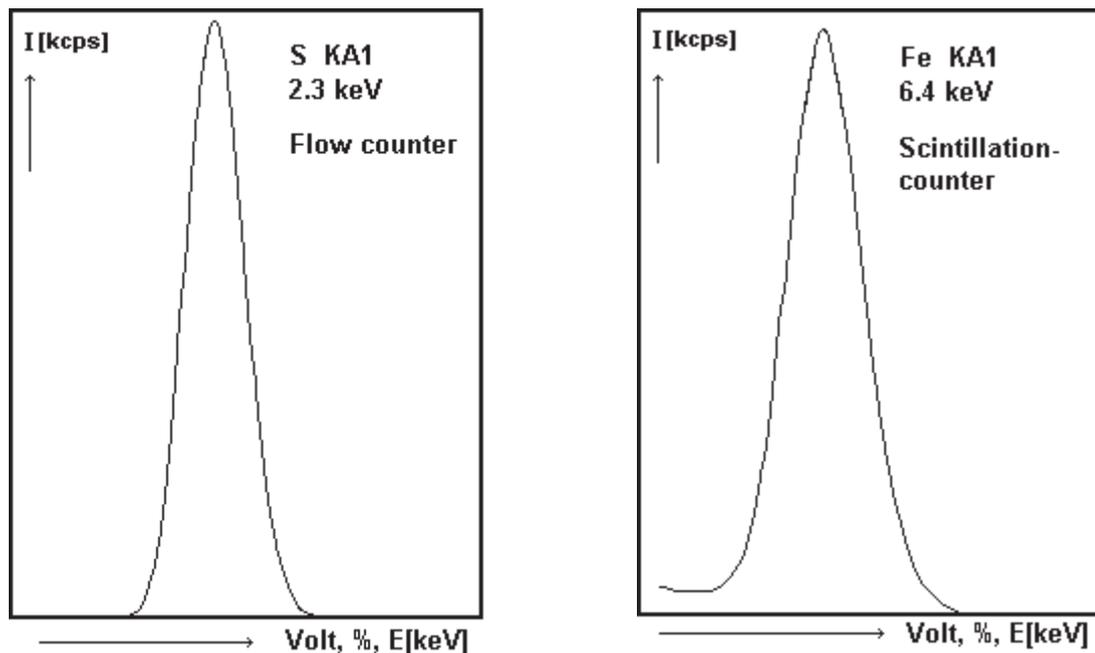


Fig. 10 (a): Pulse height distribution (S)
Gas proportional counter.

(b): Pulse height distribution (Fe)
Scintillation counter.

If argon is used as the counting-gas component in gas proportional counters (flow counters or sealed counters), an additional peak, the **escape peak** (Fig. 11), appears when X-ray energies are irradiated that are higher than the absorption edge of argon.

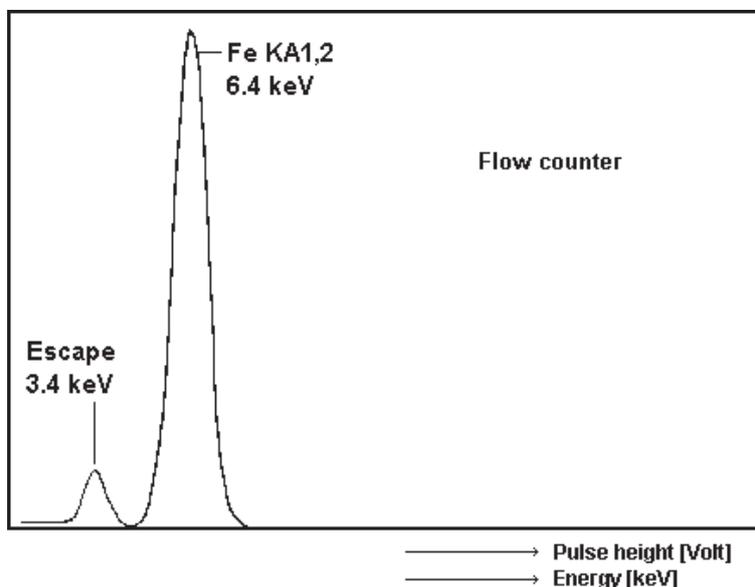


Fig. 11 (a): Pulse-height distribution (Fe) with escape peak.

The escape peak arises as follows:

The incident X-ray photon passes its energy to the counting gas thereby displacing a K electron from an argon atom. The Ar atom can now emit an Ar $K\alpha_{1,2}$ X-ray photon with an energy of 3 keV. If this Ar-fluorescence escapes from the counter then only the incident energy minus 3 keV remains for the measured signal. A second peak, the escape peak that is always 3 keV below the incident energy, appears in the pulse height distribution. Please refer to Fig. 10 (a): In this case no escape peak appears as the incident energy of sulphur radiation (S $K\alpha_{1,2}$) is lower than the absorption edge of argon.

When using other counting gases (Ne, Kr, Xe) instead of argon, the escape peaks appear with an energy difference below the incident energy that is equivalent to the appropriate emitted fluorescence radiation (Kr, Xe). Using neon as the counting-gas component produces no recognizable escape peak as the Ne K-radiation, with energy of 0.85 keV, is almost completely absorbed in the counter. Also, the energy difference to the incident energy of 0.85 keV and the fluorescence yield are very small.

The Counter Plateau

Every counter has a high-voltage area within which it can be optimally adapted to the appropriate application (operating range). It has already been mentioned that the gas amplification must be set somewhat higher for measuring light elements than for the K-radiation of heavier elements by changing the high voltage of the gas proportional counter. The high-voltage area that can be used for the application is called the "plateau" of the counter. This applies for the gas counter as well as for the scintillation counter with an integrated photomultiplier. Generally, the counter plateau is determined by irradiating X-ray energy typical for the application into the counter and measuring the intensity under increasing high voltage.

Fig. 11 (b) illustrates the example of a counter plateau for a gas proportional counter with Ar + 10 % CH₄ as counting gas and Fe $K\alpha_1$ as the radiation source (Fig. 11 (a)). The number of pulses has been applied whose pulse height (Volt) exceeds a lower electronic discriminator threshold (e.g. 100 mV). If the high voltage is too low, the electrical field strength is not sufficient for producing a gas amplification; the pulse heights are too low to pass the threshold.

If the high voltage is increased in increments, at first the pulses produced by the Fe K-peak will exceed the discriminator threshold's voltage height and be registered. If the power is increased further, the escape peak will pass the threshold, too. So, by increasing the counter high-voltage the radiation source's peaks are pushed over the discriminator threshold.

After a steep increase in intensity, a relatively flat high-voltage area takes shape. This is the counter's plateau or operating range. At the end of the plateau, the intensity increases sharply again due to counter pulses that do not primarily originate from the incident source. No measurements are to be taken in this area. Fig. 11 (b) shows a form of plateau that occurs as a result of the integral measurement of all pulses over the discriminator threshold. If the pulses are pushed over a discriminator window with a lower and upper threshold, the intensity drops once more as the peaks are pushed out of the window again.

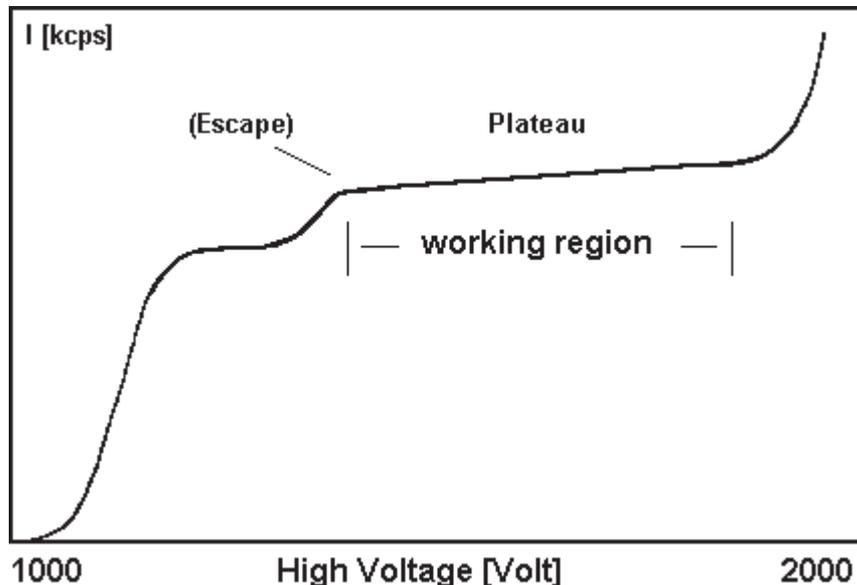


Fig. 11 (b): A gas proportional counter plateau.

Diffraction in Crystals

Interference

Electromagnetic radiation displays interference and diffraction effects due to the nature of its waves. "Interference" is the property of waves to overlap each other and, under certain circumstances, to **cancel out** or **amplify** each other.

Amplification always takes place, for example, when waves of identical wavelength have zero phase difference (coherence), i.e. when "wave maxima" and "wave minima" overlap in such a way that minima meets minima and maxima meets maxima. This is precisely the case when the phase difference $\Delta\lambda$ is zero or a multiple of the wavelength λ , i.e.:

$$\Delta\lambda = n\lambda \quad n = 0, 1, 2, \dots$$

"n" is referred to as the "order" (Fig. 12):

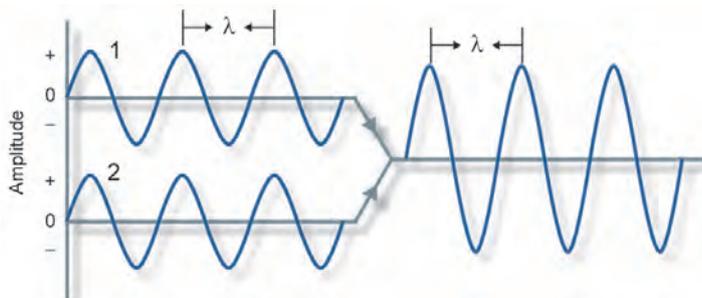


Fig. 12: Amplification resulting from the effects of interference.

Where the phase difference is one half of the wavelength: $n = 1/2, 3/2, 5/2 \dots$ wave maxima coincide with wave minima resulting in total cancellation (Fig. 13). When a number of waves of the same wavelength propagating in the same direction interfere with each other under continuous phase shift, only the coherent among them will be amplified. In total, the rest will almost completely cancel each other out.

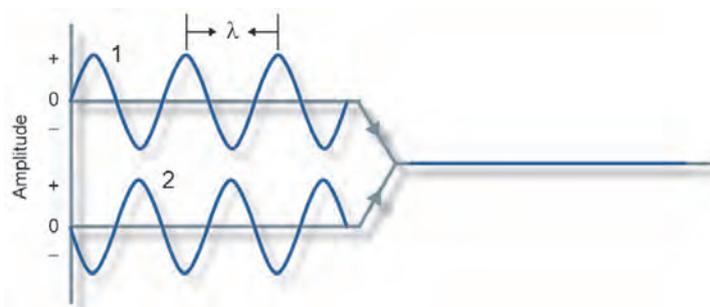


Fig. 13: Cancellation resulting from the effects of interference.

Diffraction

From what we experience every day we know that light generally travels in straight lines. This corresponds with the image of light as a beam of particles (photons). We know from waves that when a wave series (e.g. water waves) travels through a hole smaller than the wavelength, the waves exiting the hole spread out to the sides. Light displays the same characteristics due to its nature of waves. The deviation of light from its travel in a straight line is called **diffraction**, also when it is not reflected or refracted.

There are numerous applications for the effects of diffraction. In wavelength dispersive XRF we are mainly interested in diffraction in reflection grids. Often used in the optical range ($\lambda = 380 - 750 \text{ nm}$) are mirror lattices produced by spacing grooves at equal distances in reflecting metal surfaces. This is no longer possible in the X-ray field for technical reasons as the wavelengths involved are around 2 to 5 orders of magnitude smaller ($\lambda = 0.02 - 11 \text{ nm}$). Very much smaller lattice distances such as are found in natural crystals, are required for X-ray diffraction in the reflection grid.

The effects of diffraction are a prerequisite for wavelength dispersive XRF. After excitation of the elements in the sample (by X-rays), a blend of element-characteristic wavelengths (fluorescence radiation) leaves the sample. There are now two methods (or procedures) in XRF of identifying these various wavelengths. The **energy dispersive XRF** applies an energy dispersive detector that is able to resolve the different energies. **Wavelength dispersive XRF** utilizes the diffraction effects to split up (or separate) the various wavelengths in an analyzer crystal. The detector subsequently determines the intensity of a particular wavelength. The procedure will be covered in detail in the following sections.

X-ray Diffraction from a Crystal Lattice, Bragg's Equation

Crystals consist of a periodic arrangement of atoms (molecules) that form the crystal lattice. In such an arrangement of particles you generally find numerous planes running in different directions through the lattice points (=atoms, molecules), and not only horizontally and vertically but also diagonally. These are called **lattice planes**. All of the planes parallel to a lattice plane are also lattice planes and are at a defined distance from each other. This distance is called the **lattice plane distance 'd'**.

When parallel X-ray light strikes a lattice plane, every particle within it acts as a scattering centre and emits a secondary wave. All of the secondary waves combine to form a reflected wave. The same occurs on the parallel lattice planes for only very little of the X-ray wave is absorbed within the lattice plane distance 'd'. All these reflected waves **interfere** with each other. If the amplification condition "phase difference = a whole multiple of the wavelength" ($\Delta\lambda = n\lambda$) is not precisely met, the reflected wave will interfere such that cancellation occurs. All that remains is the wavelength for which the amplification condition is met precisely. For a defined wavelength and a defined lattice plane distance, this is only given with a specific angle, the **Bragg angle** (Fig. 14).

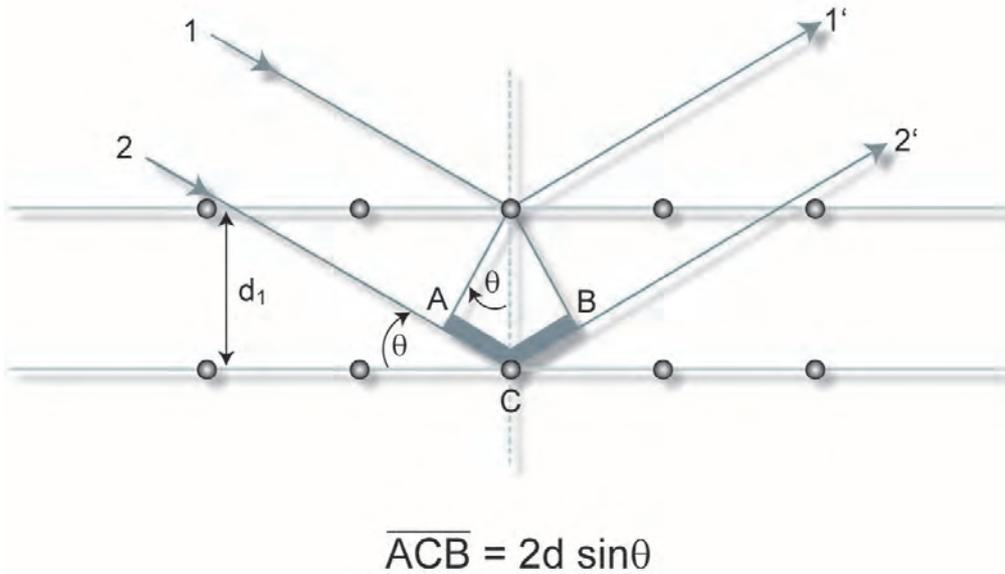


Fig. 14: Bragg's Law.

To Fig. 14:

Under amplification conditions, parallel, coherent X-ray light (1,2) falls on a crystal with a lattice plane distanced 'd' and is scattered below the angle θ (theta) (1', 2'). The proportion of the beam that is scattered on the second plane has a phase difference of 'ACB' to the proportion of the beam that was scattered at the first plane. Following the definition of the sine:

$$\frac{'AC'}{d} = \sin\theta \text{ or } 'AC' = d \sin\theta$$

The phase difference 'ACB' is twice that, so:

$$'ACB' = 2d \sin\theta$$

The amplification condition is fulfilled when the phase difference is a whole multiple of the wavelength λ , so:

$$'ACB' = n\lambda$$

This results in Bragg's Law:

$n\lambda = 2d \sin\theta$	Bragg's equation
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$n = 1, 2, 3 \dots$ Reflection order

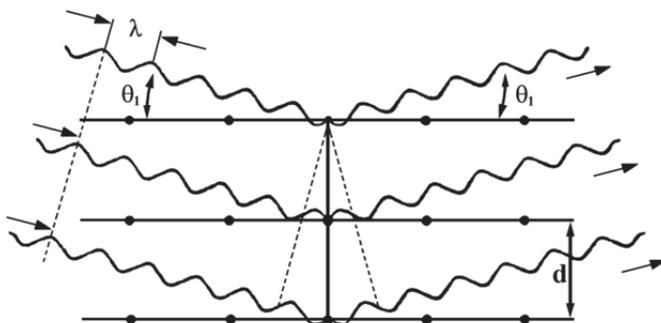


Fig. 15 (a): 1st order reflection: $\lambda = 2d \sin \theta_1$.

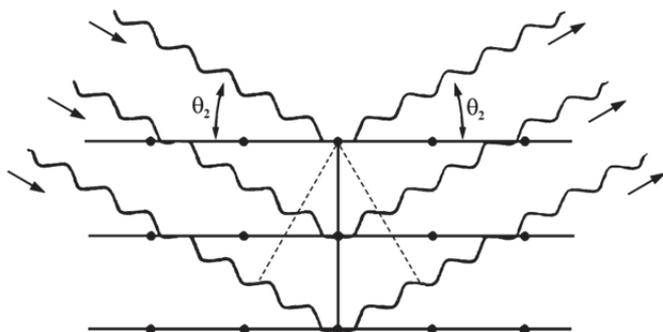


Fig. 15 (b): 2nd order reflection: $2\lambda = 2d \sin \theta_2$.

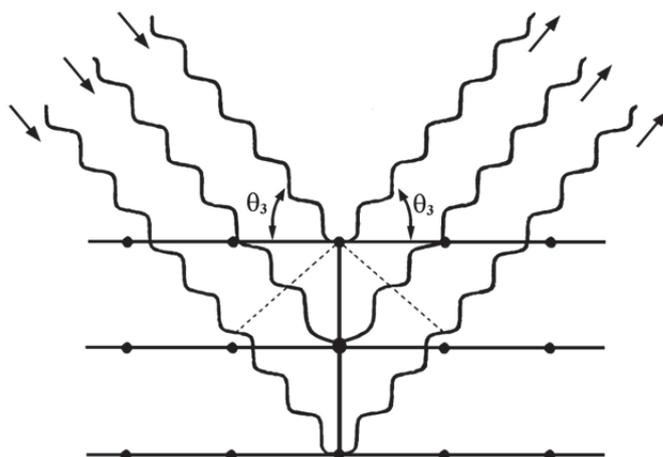


Fig. 15 (c): 3rd order reflection: $3\lambda = 2d \sin \theta_3$.

Fig. 15 (a), (b) and (c) illustrate Bragg's Law for the reflection orders $n = 1, 2, 3$.

On the basis of Bragg's Law, by measuring the angle θ , you can determine either the wavelength λ , and thus chemical elements, if the lattice plane distance 'd' is known or, if the wavelength λ is known, the lattice plane distance 'd' and thus the crystalline structure.

This provides the basis for two measuring techniques for the quantitative and qualitative determination of chemical elements (XRF) and crystalline structures (molecules, XRD), depending on whether the wavelength λ or the 2d-value is identified by measuring the angle θ (Tab. 3):

Tab. 3: Wavelength dispersive X-ray techniques.

Known	Sought	Measured	Method	Instrument type
d	λ	θ	X-ray fluorescence	Spectrometer
λ	d	θ	X-ray diffraction	Diffractometer

In X-ray diffraction (**XRD**) the sample is excited with monochromatic radiation of a known wavelength (λ) in order to evaluate the lattice plane distances as per Bragg's equation.

In **XRF**, the 'd'-value of the analyzer crystal is known and we can solve Bragg's equation for the element-characteristic wavelength (λ).

Reflections of Higher Orders

Fig. 15 (a) – (c) illustrate the reflections of the 1st, 2nd, and 3rd order of **one** wavelength below the different angles $\theta_1, \theta_2, \theta_3$. Here, the total reflection is made up of the various reflection orders (1, 2,

n). The higher the reflection order, the lower the intensity of the reflected proportion of radiation generally is. How great the maximum detectable order is depends on the wavelength, the type of crystal used and the angular range of the spectrometer.

It can be seen from Bragg's equation that the product of reflection order 'n = 1, 2, ...' and wavelength 'λ' for greater orders, and shorter wavelengths 'λ* < λ' that satisfy the condition 'λ* = λ/n', give the same result.

Accordingly, radiation with one half, one third, one quarter etc. of the appropriate wavelength (using the same type of crystal) is reflected below an **identical angle 'θ'**:

$$1\lambda = 2(\lambda/2) = 3(\lambda/3) = 4(\lambda/4) = \dots\dots\dots$$

As the radiation with one half of the wavelength has twice the energy, the radiation with one third of the wavelength three times the energy etc., peaks of twice, three times the energy etc. can occur in the pulse height spectrum (=energy spectrum) as long as appropriate radiation sources (elements) exist (Fig. 16).

Fig. 16 shows the pulse height distribution of the flow counter using the example of the element hafnium (Hf) in a sample with a high proportion of zircon. The Zr Kα₁ – peak has twice the energy of the Hf Lα₁ – peak and appears, when the Hf Lα₁ – peak is set, at the same angle in the pulse height spectrum.

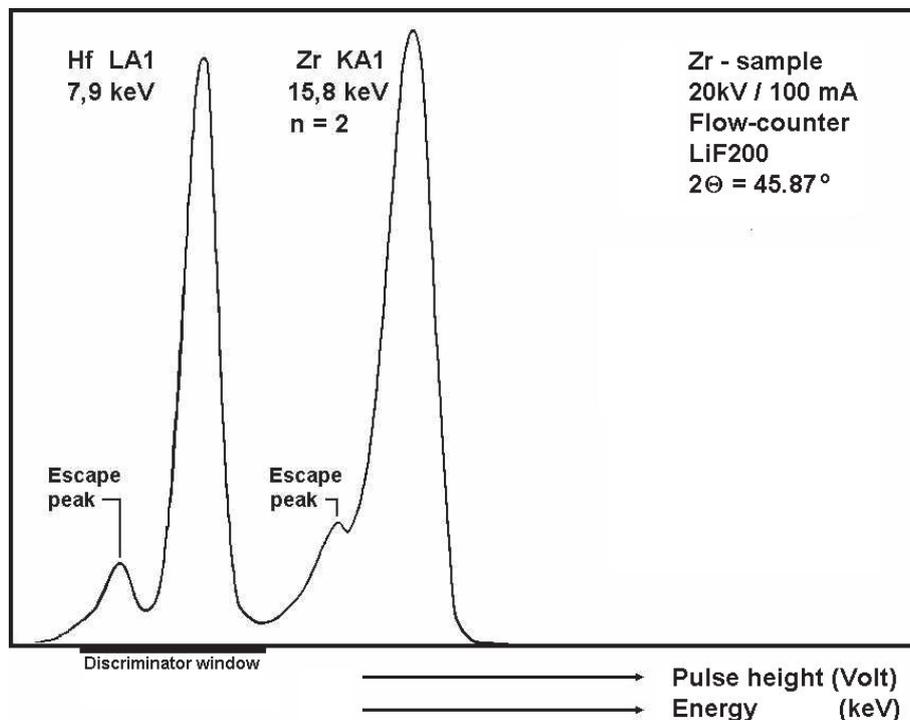


Fig. 16: 2nd order reflection (n=2).

Crystal Types

The wavelength dispersive X-ray fluorescence technique can detect every element above the atomic number 4 (Be). The wavelengths cover the range of values of four magnitudes: 0.01 - 11.3 nm (cf. Tab. 1). As the angle θ can theoretically only be between 0° and 90° (in practice 2° to 75°), 'sin θ' only accepts values between 0 and +1. When Bragg's equation is applied:

$$0 < \frac{n\lambda}{2d} = \sin \theta < +1$$

This means that the detectable element range is limited for a crystal with a lattice plane difference 'd'. Therefore a variety of crystal types with different '2d' values is necessary to detect the whole element range (from atomic number 4).

Tab. 4 shows a list of the common crystal types.

Lithium fluoride crystals which also state the lattice planes (200, 220, 420) are identical to the following names:

LiF(420) = LiF(210)

LiF(220) = LiF(110)

LiF(200) = LiF(100)

Besides the 2d-values, the following selection criteria must be considered when a particular type of crystal is to be used for a specific application:

- resolution
- reflectivity (--> intensity)

Further criteria can be:

- temperature stability
- suppression of higher orders
- crystal fluorescence

Tab. 4: Crystal types.

Crystal	Name	Element range	2d-value (nm)
LiF(420)	Lithiumfluoride	≥ Co Kβ ₁	0.1801
LiF(220)	Lithiumfluoride	≥ V Kα ₁	0.2848
LiF(200)	Lithiumfluoride	≥ K Kα ₁	0.4028
XS-400	Lithiumfluoride	≥ K Kα ₁	0.4028
Ge, XS-Ge-C	Germanium	P, S, Cl	0.653
XS-CEM	Multilayer	Al, Si, P, S	Trade secret
InSb, XS-InSb-C	Indiumantimonide	Si	0.7481
PET, XS-PET-C	Pentaerythrite	Al – Ti	0.874
AdP	Ammoniumdihydrogenphosphate	Mg	1.0648
TIAP	Thalliumhydrogenphthalate	F, Na	2.5760
XS-55	Multilayer [W/Si]	O - Si (C)	5.5
XS-N	Multilayer [Ni/BN]	N	11
XS-C	Multilayer [TiO ₂ /C]	C	12
XS-B	Multilayer [La/B ₄ C]	B (Be)	20

Dispersion, Line Separation

The extent of the change in angle $\Delta\theta$ upon changing the wavelength by the amount $\Delta\lambda$ (thus: $\Delta\theta/\Delta\lambda$) is called "dispersion". The greater the dispersion, the better is the separation of two adjacent or overlapping peaks. Resolution is determined by the dispersion as well as by surface quality and the purity of the crystal.

Mathematically, the dispersion can be obtained from the differentiation of the Bragg equation:

$$\frac{d\theta}{d\lambda} = \frac{n}{2d \cos \theta}$$

It can be seen from this equation that the dispersion (or peak separation) increases as the lattice plane distance 'd' declines.

Examples: (cf. Tab. 5)

The 2θ -values of the $K\alpha_1$ -peaks of vanadium (V) and chromium (Cr) are further apart when measuring with LiF(220) than when measuring with LiF(200).

The 2θ -values of the $K\alpha_1$ -peaks of sulphur (S) and phosphorus (P) are further apart when measuring with the Ge crystal than when doing so with the PET crystal (cf. e.g.: Bruker AXS table-top periodic table).

Tab. 5: Explanatory details for dispersion.

Crystal type	2d-value (nm)	2θ (EI1) (degrees)	2θ (EI2) (degrees)	Difference (degrees)
LiF(220)	0.2848	107.11 (Cr)	123.17 (V)	16.06
LiF(200)	0.4028	69.34 (Cr)	76.92 (V)	7.58
Ge	0.653	110.69 (S)	141.03 (P)	30.34
PET	0.874	75.85 (S)	89.56 (P)	13.71

The following describes the characteristics of the individual crystal types divided into “standard crystals”, “multilayers” and “special crystals”.

Standard Types, Multilayers

LiF(200), LiF(220), LiF(420):

LiF crystal types exist in a variety of lattice planes (200/220/420). In the sequence (200) \rightarrow (220) \rightarrow (420), resolution increases and reflectivity decreases (Fig. 17).

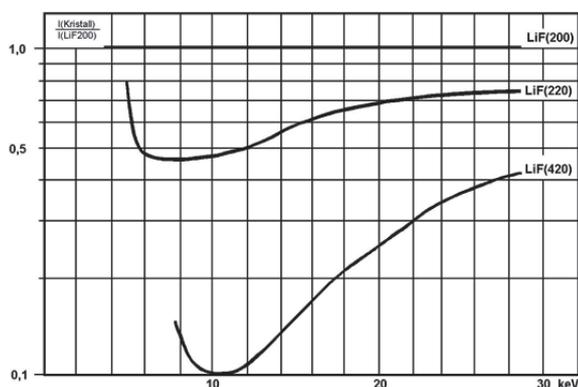


Fig. 17: Intensities of the crystals LiF(220) and LiF(420) in relation to LiF(200). (Intensity LiF(200) = 1).

LiF(200):

A universally usable crystal for the element range atomic number 19 (K) onwards; high reflectivity, high sensitivity (HS).

LiF(220):

Lower reflectivity than the LiF(200) but higher resolution (HR); can be used for the element range atomic number 23 (V) onwards; particularly suitable for better peak separation where peaks overlap.

Examples for the application of the LiF(220) for reducing peak overlaps:

Cr	$K\alpha_{1,2}$	-	V	$K\beta_1$
Mn	$K\alpha_{1,2}$	-	Cr	$K\beta_1$
U	$L\alpha_1$	-	Rb	$K\alpha_{1,2}$

LiF(420):

One of the special crystals; can be used for the element range atomic number 28 (Ni or Co $K\beta_1$) onwards; best resolution but low reflectivity;

Fig. 17 shows a reflectivity of only 10 % of that of the LiF(200) for the LiF(420) in the energy range around 10 keV.

PET:

A universal crystal for the elements Al to Ti (K-peaks) and Rb to I (L-peaks).



Caution

The PET is the crystal with the greatest heat-expansion coefficients, i.e. temperature fluctuations are most noticeable here.

Multilayers XS-55, XS-CEM, XS-N, XS-C, XS-B:

Multilayers are not natural crystals but artificially produced 'layer analyzers'. The lattice plane distances 'd' are produced by applying thin layers of two materials in alternation on to a substrate (Fig. 18). Multilayers are characterized by high reflectivity and a somewhat reduced resolution. For the analysis of light elements the multilayer technique presents an almost revolutionary improvement for numerous applications in comparison to natural crystals with large lattice plane distances (e.g. RbAP, PbST, KAP).

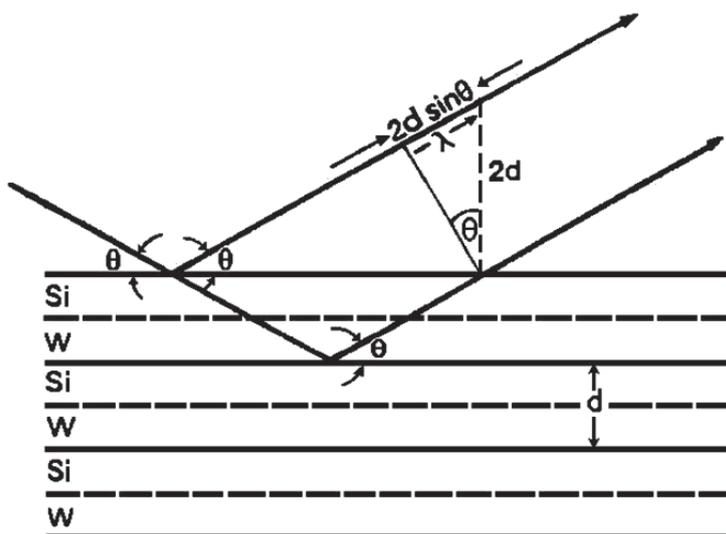


Fig. 18: Diffraction in the layers (here: Si/W) of a multilayer.

XS-55:

The most commonly used multilayer with a 2d-value of 5.5 nm for analyzing the elements N (C) to Si; standard application for measuring the elements F, Na, Mg.

Special Crystals

The term 'special crystals' refers to crystal types and multilayers that are not used universally but are employed in special applications.

LiF(420):

Cf. 'standard types', description of the LiF crystals (200, 220, 420).

XS-400:

The XS-400 is a specific LiF200 type crystal which improves the intensity over the whole element range starting from K α by more than 30 %

Ge:

A very good crystal for measuring the elements S, P, Cl. In comparison to PET, Ge is characterized by a higher dispersion and a more stable temperature behavior. Ge suppresses the peaks of the 2nd and 4th order, in particular.

Ge is especially suitable for differentiating between sulphide/sulphate e.g., in samples of cement.

XS-Ge-C:

The XS-Ge-C is a specific germanium crystal, laterally curved to improve the sensitivity for P by 40 % and for S by 20 %.

XS-CEM:

The XS-CEM is a multilayer crystal for minor and major concentration ranges to give long term stable data without degradation by time, like the organic crystal PET.

AdP:

In practice, AdP is only used for the analysis of Mg and has a higher resolution with a significantly lower reflectivity compared to the multilayer XS-55. AdP is therefore required where interference peaks can occur such as in the case of low Mg concentrations in an Al matrix.

TIAP:

The TIAP has high resolution but low reflectivity and is recommended for analyzing F and Na if the resolution of XS-55 is insufficient (e.g. where Na is overlapped by the Zn-L peaks in Zn-rich samples).

**Danger**

Disadvantages are the limited lifetime, toxicity, and high price.

InSb:

The InSb is a very good crystal for analyzing Si in traces as well as in higher concentrations (e.g. glass). It replaces PET and is used wherever high precision and great stability is required. The disadvantages are the limited use (only Si) and the high price.

XS-C:

The XS-C is a multilayer with a 2d-value of 12 nm, specially optimized for carbon.

XS-N:

The XS-N is multilayer with a 2d-value of 11 nm, specially optimized for nitrogen.

XS-B:

The XS-B is multilayer with a 2d-value of 20 nm, specially optimized for boron and is equally suitable for the analysis of Be.

Which multilayer crystal is the most suitable for analyzing the very light elements?

Fig. 19 (a) shows that the XS-B is the best one for analyzing Boron (B), naturally with the corresponding coarse collimator (at least 2° opening).

For the analysis of Carbon (C) the XS-C provides a sharper peak and a better ratio of the peak / background intensities, which means that better sensitivities can be achieved (Fig. 19 (b)). To apply the XS-55 for analyzing Carbon should be exceptional in case of having no XS-C. Only very high concentrations (several tens of per cent) of Carbon can be determined with the XS-C. In case of determining Carbon with the XS-55 using the „standardless“ precalibrated XRF routine, please don't forget to select a very slow scanning speed (long measuring time) for Carbon or to select the peak/background measurement mode.

Nitrogen (N) is best analyzed using the XS-N. If needed the XS-55 can be applied also for nitrogen (Fig. 19 (c)). XS-B and XS-C are not suitable to analyze Nitrogen.

Oxygen (O) and all further „heavier“ light elements have to be analyzed with the XS-55 which gives the best resolution and the best peak/background ratio (Fig. 19 (d)).

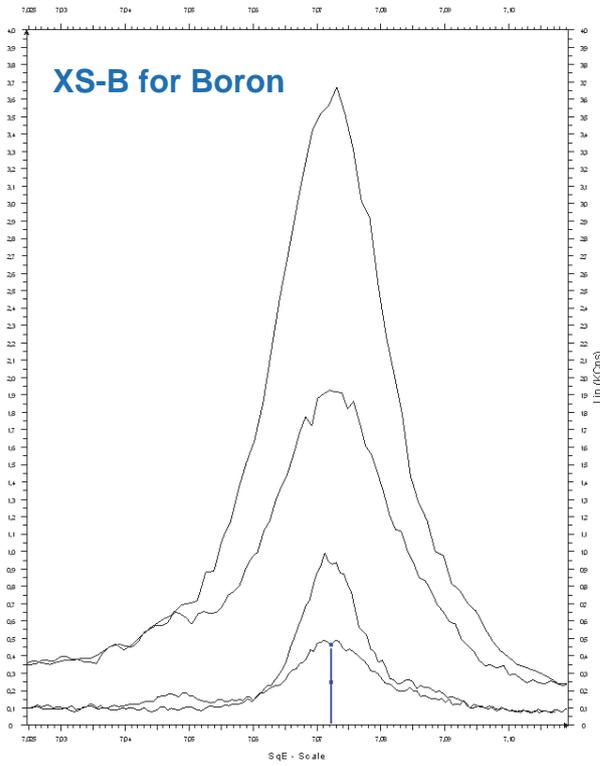


Fig. 19 (a): XS-B is the best multilayer crystal for analyzing Boron (B).

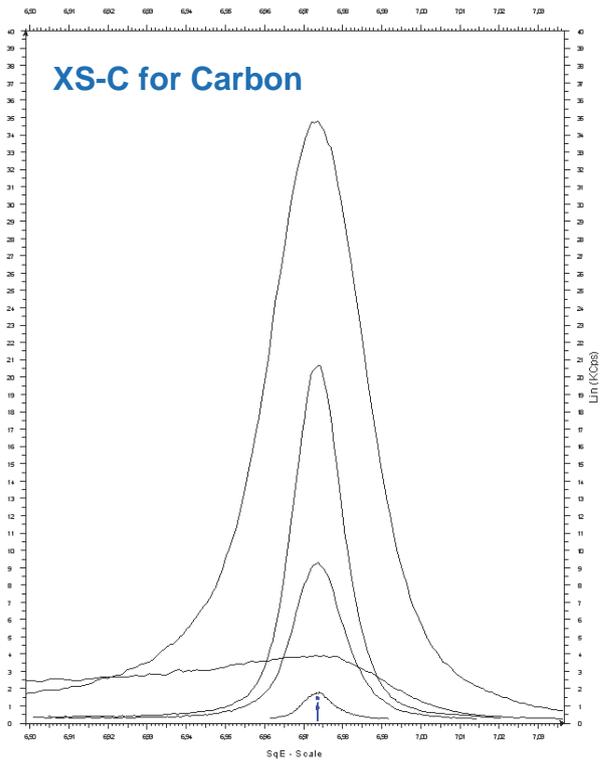


Fig. 19 (b): The XS-C multilayer crystal is suitable for the determination of Carbon.

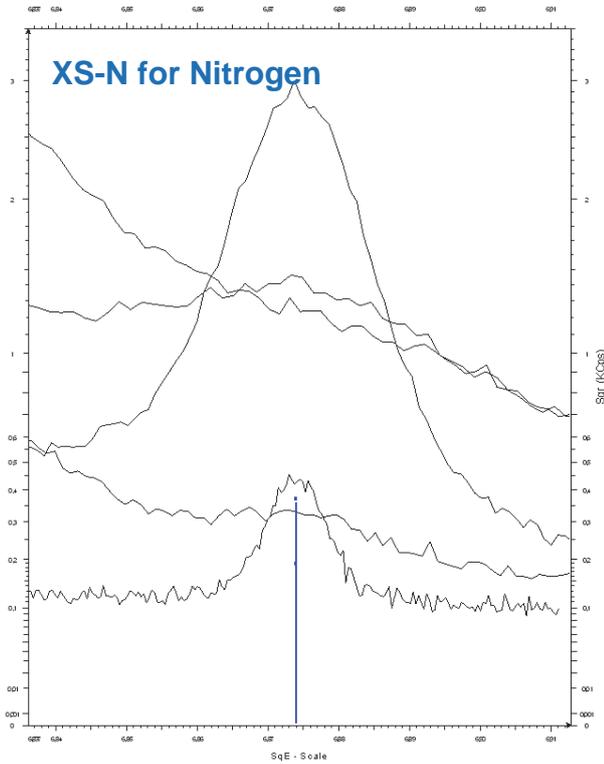


Fig. 19 (c): Nitrogen (N) is best analyzed using the XS-N.

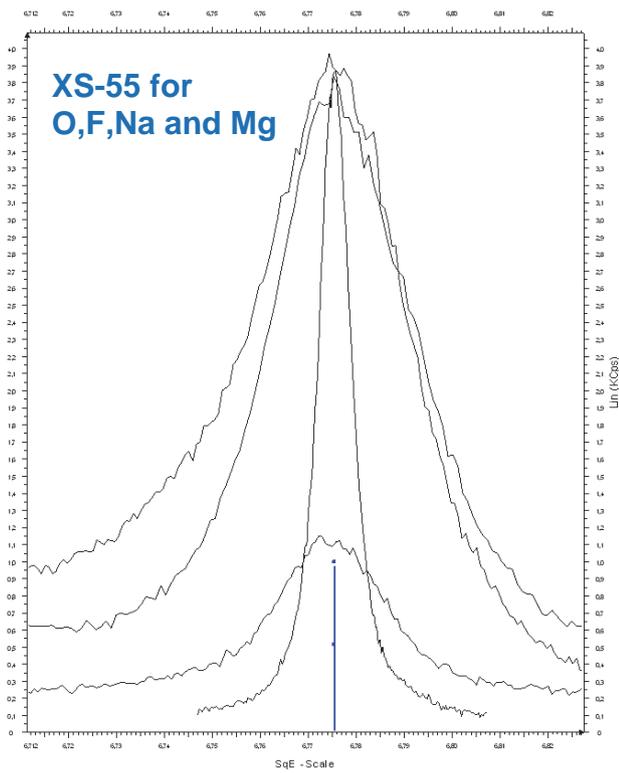


Fig. 19 (d): Oxygen (O) and all further „heavier“ light elements have to be analyzed with the XS-55.

Curved Crystals for Rowland Geometry

Whereas flat and laterally curved crystals are used in sequence spectrometers, multichannel spectrometers principally employ curved crystals (cf. instrumentation, Fig. 22 - Fig. 25).

The curvature of the crystals is selected in such a way that by applying a slit optics the X-ray entrance slit is focused by the curved crystals onto the exit slit. This allows higher intensities in a space-saving geometric arrangement.

Different types of crystal curvature are used for focusing. The most commonly used are the curvatures that follow a logarithmic spiral (Fig. 20 (a)) and the Johansson curvature (including grinding) (Fig. 20 (b)).

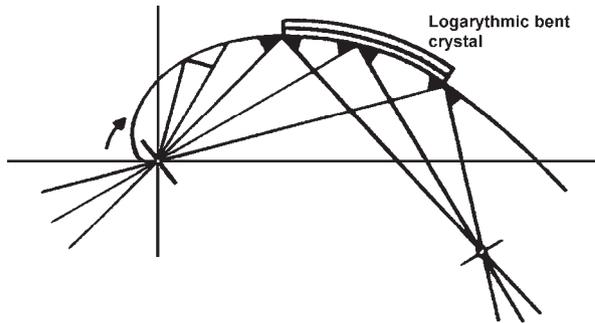


Fig. 20 (a): Logarithmic spiral curvature.

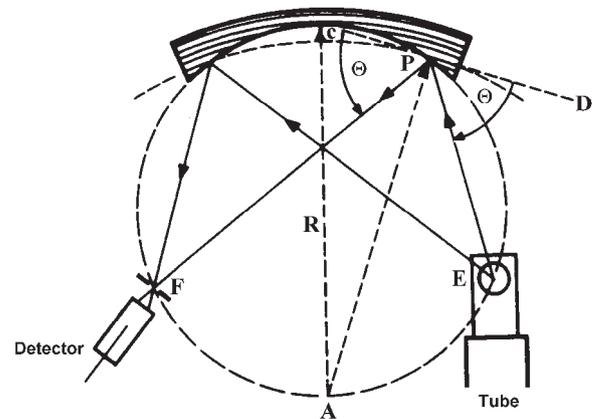


Fig. 20 (b): Johansson curvature.

Instrumentation

For X-ray fluorescence analysis two different kinds of instruments are being used. Systems based on energy dispersive detection of X-ray fluorescence radiation are typically smaller in benchtop size down to mobile hand use and cost attractive. The main uses are dedicated material specific applications or general monitoring. Wavelength dispersive systems are widely used for challenging applications enabling very accurate, fast and precise process and quality control applications in industry. The main difference in technologies and applications are explained in this chapter.

Wavelength Dispersive X-ray Fluorescence Spectrometers

The following text explains the wavelength dispersive X-ray fluorescence spectrometer instrumentation of Bruker AXS. The first section contains brief summaries on the multichannel X-ray spectrometer S8 LION. The next section deals in detail with the technology of the sequential spectrometers S8 TIGER. The final section will handle common technologies such as detectors,...

The Multichannel Spectrometer S8 LION

The multichannel spectrometer S8 LION can measure up to 16 elements simultaneously. A multichannel spectrometer is always required where short measuring periods are necessary when analyzing large numbers of elements, or a high throughput of samples (e.g. 600 samples per day) must be dealt with as in industrial quality and production control processes.

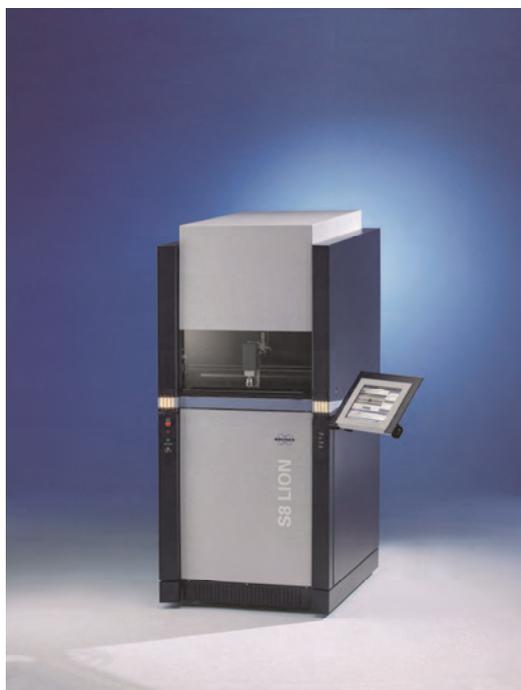


Fig. 21: Multichannel Spectrometer S8 LION

An individual measuring channel incorporating crystal, detector and electronics module must be installed for each element line. As there are limited possibilities for the geometric arrangement of 16 channels in close proximity to the sample, so-called **monochromators** with **slit-optics** are used. A monochromator comprises an arrangement of entry slit, curved focusing crystal and an exit slit (Fig. 22, Fig. 23). The crystals are curved in a logarithmic spiral and focus the desired wavelength of the beam passing through the entry slit on to the exit slit. The detector is located behind the exit slit. Scintillation counters or gas proportional counters are used depending on the element line. Flow counters as well as sealed proportional counters can be used as gas proportional counters. Sealed proportional counters can be equipped with a 25 μm Be or an SHT (Super-High Transmission)

window. The 25 μm thin Be window is used for the elements Al - Fe. The new SHT window is used for the elements Be to Mg.

All monochromators are located around the compact sample chamber, which has always vacuum.. The beam is applied from above. The fixed channels are used exclusively for quantitative analyses. A scanner can be employed for qualitative analysis.

As all elements are measured simultaneously, a generator setting (kV/mA) must be selected that provides the best compromise in each case for the components to be measured. The measurement period depends on statistical accuracy requirements of the element with the lowest intensity and is typically around 20 – 60 seconds. No background positions can be measured as the monochromators are at a fixed setting to the angle of the appropriate line.

When measuring trace and major elements simultaneously, the generator is normally set so that the trace elements can be measured with the highest possible intensity. This means that the major elements are usually of very high intensity that cannot be processed by the detectors. For cases such as these, the S8 LION can be fitted with attenuators for the major elements whose intensities are reduced sufficiently for them to then lie in the operational range of the detectors.

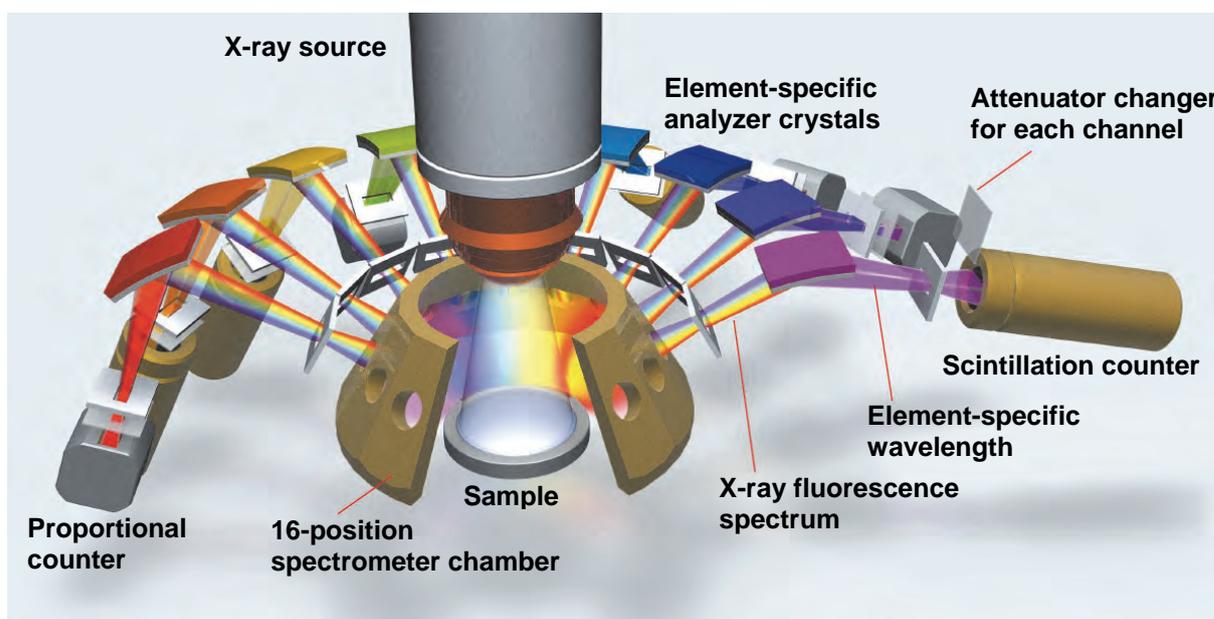


Fig. 22: Beam entry in the S8 LION.



Fig. 23: Monochromator with crystal, attenuator and detector.

The Sequential Spectrometer S8 TIGER

The heart of the spectrometer is a high-precision goniometer with two independent stepper motors for separate $\theta/2\theta$ drive.

The functions and processes inside the spectrometer are controlled with modern electronics. A central processing unit (CPU) coordinates the internal flow of information and communicates with the external analysis computer (PC) or the TouchControl interface. Having its own service interface enables the master processor be remote-diagnosed by the Bruker AXS-Service-Centers via Teleservice or WEBEX, without being able to access security-relevant data in the analysis computer. This concept optimizes the diagnosis possibilities and rapid fault location.



Fig. 24: Sequential Spectrometer S8 TIGER

The various measuring parameters are set exclusively via the analysis computer's software and provide the user with great flexibility.

The separate $\theta/2\theta$ -goniometer drive with two independent stepper motors allows a precise $\theta/2\theta$ -angle alignment via the analysis computer's software.

The flow counter is situated inside the spectrometer chamber and has an angle scope of 0° to 115° . Located behind the flow counter and outside the chamber, separated by a 0.1 mm Al foil, is the scintillation counter with an angle scope of 17 - 152° . Both detectors can be used individually or in tandem. In tandem operation, the intensity in the flow counter is measured as well as the radiation that passes through the flow counter and the radiation that is absorbed by the scintillation counter.

Integrating temperature measuring points allows this stability-relevant factor to be checked in the instrument. Furthermore, the temperature of the water in the internal deionized cooling system is kept constant.

An optional protractible/retractable foil screen can be installed between the sample chamber and the spectrometer chamber for measuring, for example, liquids in a He atmosphere.

Fig. 25 shows the beam path of the S8 TIGER.

A flexible, modifiable sample changer with a robot arm that moves in the directions X and Y allows fully automatic transport of:

- sample cups with a magnetic grabber
- 'bare samples' with a suction unit
- combinations of both
- steel rings with a magnetic holder

to the instrument's sample chamber position.

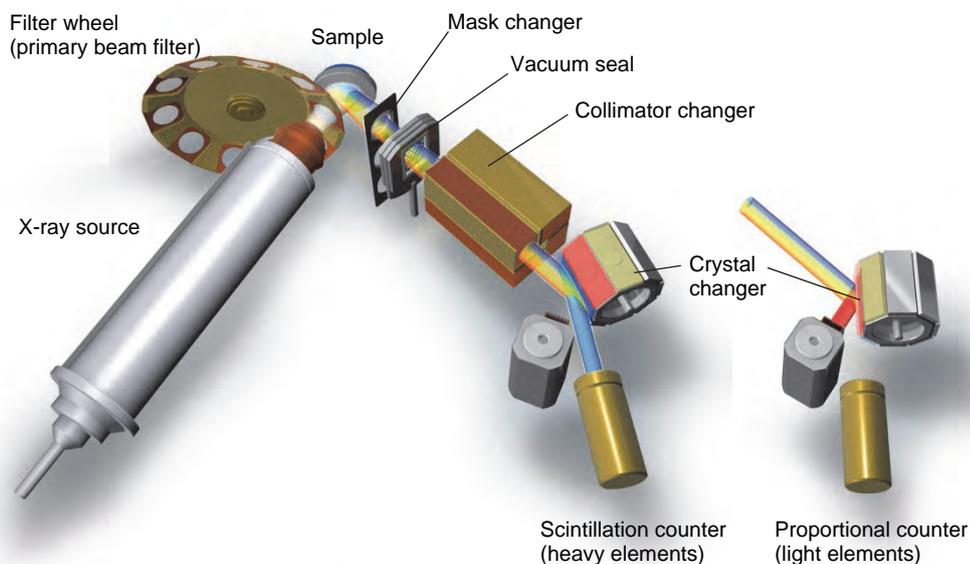


Fig. 25: Beam path in the S8 TIGER.

Problem-free docking on to a conveyor belt allows easy integration into an automated environment. The function and possible settings for the various parameters will now be described in the order they are encountered by the beam propagating from the tube to the scintillation counter.

The End-window Tube and the Generator

The tube and generator are designed for a permanent maximum output of 4 kW (S8 TIGER 4K) at a maximum high voltage of 60 kV and a maximum tube current of 170 mA. The combination of high voltage and tube current must not exceed 4 kW, e.g. at 4 kW max.:

- 24 kV / 170 mA = 4.08 kW
- 27 kV / 150 mA = 4.05 kW
- 30 kV / 134 mA = 4.02 kW
- 40 kV / 100 mA = 4.00 kW
- 50 kV / 80 mA = 4.00 kW
- 60 kV / 67 mA = 4.02 kW

Minimum settings: 20 kV / 5 mA = 0.1 kW



Note

The control and analysis software SPECTRA^{plus} checks the settings and prevents the maximum permissible values being exceeded.

Rhodium is used as the standard anode material. The light elements Be to Cl are effectively excited by the Rh-L beam's high transmission rate through the 75 μm Be tube window. The characteristic Rh-K radiation excites the elements up to Mo (Ru). The elements from Rh onwards are excited by the Bremsstrahlung's high-energy "tail".

4 kW-tubes with other anode materials can be used for special applications (e.g., Mo, W, Au, Cr).

The Primary Beam Filter

The primary beam filter is seated on a changer for 10 positions (including vacant positions) and is equipped with a selection of absorber foils. It is located between the tube and the sample and serves the purpose of filtering out undesirable or interfering components of the **tube radiation** for certain applications and improves the signal-to-noise ratio. Al and Cu foils, for example, are used in a variety of thickness as absorbers. The one fitted can be selected to suit individual requirements when purchasing the instrument.

When measuring Rh K with the Rh tube, the characteristic Rh radiation coming from the tube must be filtered out because it would otherwise be measured as a result of elastic scattering on the sample (cf. page 9). By using a 0.2 mm-thick Cu filter, the characteristic Rh tube radiation is largely absorbed prior to reaching the sample. The measurement must be taken with a tube high-voltage of 60 kV as the Rh in the sample is only excited by the high-energy Bremsstrahlung.

Fig. 27 illustrates the tube spectrum acting on the sample without a primary beam filter and tube high-voltage of 60 kV.

Fig. 28 shows the reduction in Rh radiation scattering on a plant sample using different primary beam filters made of copper or aluminum.

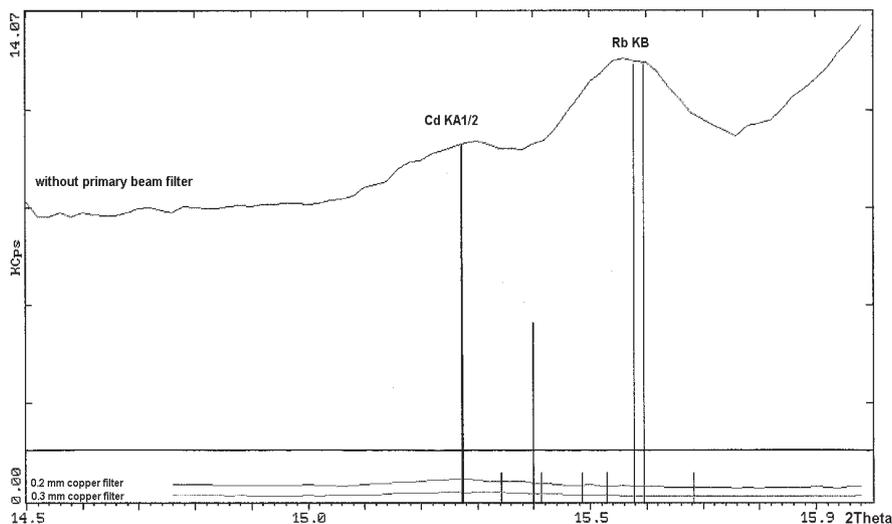


Fig. 26: Cd- and Rh-peak without a copper primary beam filter.

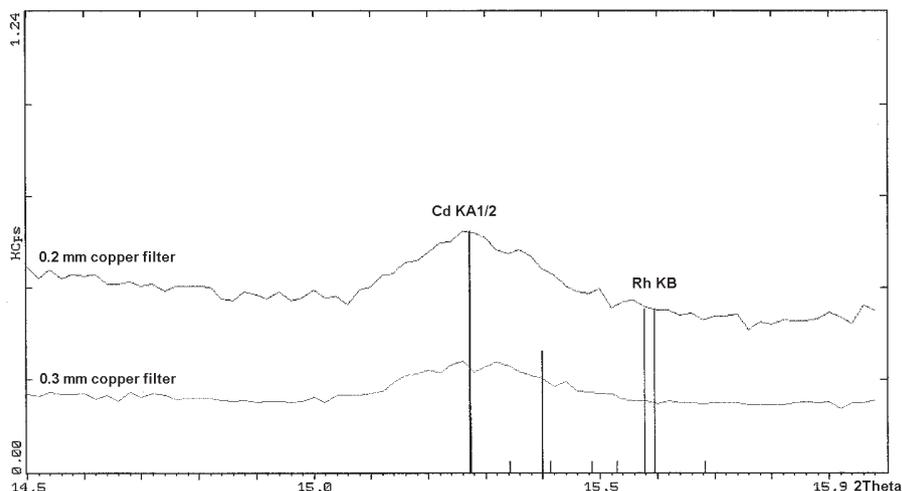


Fig. 27: Cd- and Rh-peak with 0.2 or 0.3 copper primary-beam filter.

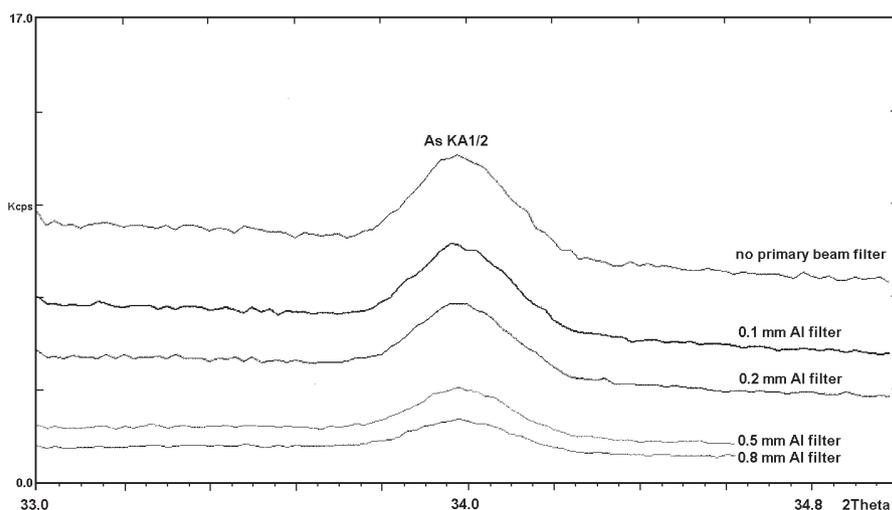


Fig. 28: The effect of the aluminum primary beam filter for optimizing the peak-background ratio.

When analyzing a sample of very pure graphite, peaks of the elements Cr, Fe, Ni and Cu can occur and in the 2θ -spectrum although the sample contains none of the elements. The Cu peak originates from the excitation of the collimator material that mainly consists of copper.

The Cr, Fe and Ni peaks are called “spectral impurities” of the tube. If the elements Cr, Fe and Ni are to be measured as traces, it may be advantageous to use the 0.2 mm Al filter to absorb these components.

Sample Cups, the Cup Aperture

In the S8 TIGER, the sample to be measured is fed directly into the measuring position where it rotates up to 30 revs per minute, depending on the application, to even out sample inhomogeneity. In the S8 TIGER the collimator mask's optimized screening allows steel apertures to be used in the majority of cases. Other aperture diameters and materials are available on request and can be placed either manually or via the automated mask changer.

Depending on type of sample magazine, the samples have to be placed in the cups manually (magazine with grab) or the magazine is designed for “bare samples” (magazine with sucker) or steel rings (magazine with magnet) which put the sample into the cup automatically. When using thin filters for measurements it must be ensured that an anti-background scattering cup is used to eliminate the fixing plate radiation. The EasyLoad changer will handle automation samples in steel rings with a diameter of 51.5 mm directly. Regular samples are placed in rings and loaded via tray. The grabber will recognize for this version, if the sample is a liquid cup by height and automatically disable the vacuum mode to avoid spillage.

The Vacuum Seal

When measuring (liquid) samples in a helium atmosphere, the vacuum can be maintained in the spectrometer volume by inserting a thin separating, or sealing, foil between the sample chamber and the spectrometer chamber. This causes the separating foil to absorb less radiation than would be the case if the spectrometer chamber were filled with helium.

For alternate measurements of samples in a vacuum and helium, this technique considerably quickens the change from one operating mode to another as a result of the smaller sluicing volume and reduces the helium consumption.

Collimator Masks

The collimator masks are situated between the sample and collimator and serve the purpose of cutting out the radiation coming from the edge of the cup aperture. The size of the mask is generally adapted to suit of the cup aperture being used. The S8 TIGER changer has 3 positions; additional masks can be placed manually very close to the sample and therefore optimally screens the sample cup aperture.

Collimators, the Soller Slit

Collimators consist of a row of parallel slats and select a parallel beam of X-rays coming from the sample and striking the crystal. The spaces between the slats determine the degree of parallelism and thus the angle resolution of the collimator.

The S8 TIGER is fitted with a 4-position changer. Besides the standard collimators with aperture angles of 0.23 and 0.46 two additional collimators can be installed to optimize the measurement parameters, depending on the application. A 0.17° and a 0.12° collimator are available for high-resolution measurements (e.g. with LiF(420)). Collimators with a low resolution 1.0° and 2.0° are advantageous for light elements such as Be, B and C as the XS-Multilayer's angle resolution is limited. Using a collimator with a low resolution increases then intensity significantly. This enables intensity to be increased without a loss in angle resolution when analyzing the light elements (Fig. 31).

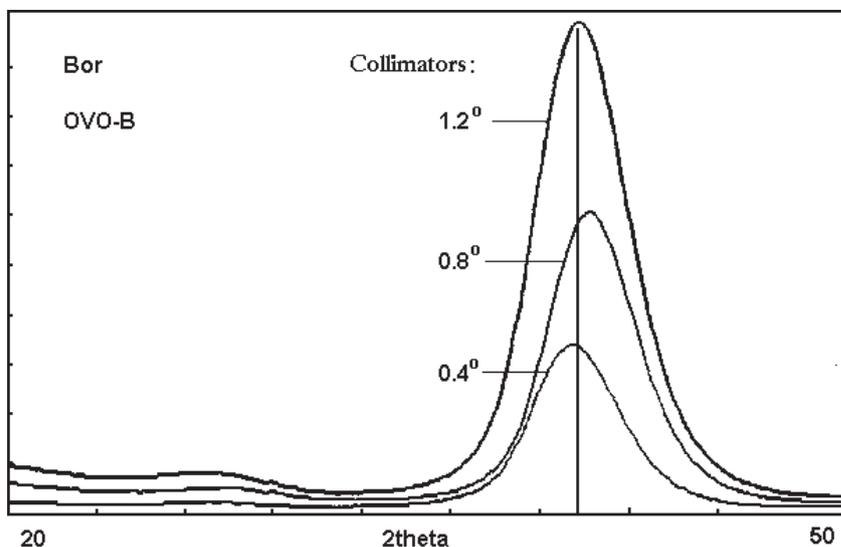


Fig. 29: The influence of collimator resolution on the intensity for light elements.

The Crystal Changer

The S8 TIGER's crystal changer can hold up to 8 crystals and be custom-equipped to suit the requirements of specific fields of application.

The Flow Counter

The flow counter is located inside the vacuum chamber and has an entrance window made of a thin, aluminum-coated foil that be selected with a thickness of 0.6 μm or 0.3 μm .

This allows optimum measurement of the light elements Be to Na. Fig. 30 illustrates the permeability for a variety of counting-tube foils that were used in older instruments. It can be seen from the transmission curve, for example, that the permeability of the 1 μm polypropylene foil for Na is around twice that of the 2 μm Makrofol-foil.

Caution



As the plastic foils have a high proportion of carbon, the absorption of the nitrogen radiation close to the C absorption edge is very high. This means that even the 1 μm foil only has an approx. 10 % permeability. For this reason, the measured intensities for the element N are relatively low. The newer 0.6 μm and especially the 0.3 μm foils are more permeable to nitrogen radiation.

Generally, Ar + 10 % CH₄ is used as the counting gas (P10). The flow of counting gas is held constant in the instrument as a fluctuating counting-gas density in the counting tube would cause fluctuations in the absorption depth as well as fluctuations in the gas amplification and thus in the position of the peaks in the pulse height spectrum, too (cf. Fundamental Principles: The gas proportional counter Fig. 8). In explosion proof laboratories in addition P5 gas can be used.

The high voltage at the counting wire is set higher for light elements (XS Multilayer) than for measuring the K-radiation (e.g. LiF crystals) of medium and heavy elements. In sequential spectrometers the detector high voltage is set separately for each element range (energy range) and thus for each installed crystal (cf. also Fig. 8).

The Scintillation Counter

The scintillation counter is positioned behind the flow counter **outside** the vacuum chamber. The radiation measured inside it must pass through the flow counter, a 0.1 mm thick vacuum-chamber

sealing foil and a 0.2 mm Be entrance window. It therefore makes sense to use the scintillation counter for energies above approx. 4.5 keV (Cr $K\alpha_1$) as the lower ones are absorbed mainly in the flow counter (cf. Fundamental Principle: The scintillation counter Fig. 9).

In the S8 TIGER the scintillation counter is directly beside the proportional counter in the spectrometer chamber and can be moved from 17° to 152°.

Electronic Pulse Processing

The pulses produced in the detectors by X-rays are processed and counted by subsequent electronic processing. The flow counter's signals are electronically amplified in a preamplifier, shaped and further processed as voltage pulses in a main amplifier (sine amplifier) and discriminator. After the photomultiplier, the scintillation counter's signals are fed directly into a main amplifier and discriminator.

The Discriminator

Depending on the application, higher order peaks or other sources of interference appear in the pulse height distribution, or the detectors' energy spectrum (cf. also Fig. 10a, b and Fig. 11) with different levels of energy. A discriminator window is used to set a lower and an upper pulse-height threshold. Only the pulse heights that lie within these limits are counted. In this way, higher order peaks or interference radiation with pulse heights beyond the window are suppressed (cf. Fig. 16). Discriminating undesirable pulses reduces the background.

Main Amplifier, Sine Amplifier

After the preamplifier (flow counter and proportional counter), or photomultiplier (scintillation counter), the pulses are further enhanced electronically in a main amplifier. As the detectors' high voltage is set separately for each crystal, i.e. as the gas amplification in the flow counter and proportional counter, or the photomultiplier's amplification, depends indirectly on the crystal, the electronic additional amplification must also be made dependent on the crystal used.

X-ray energies, for example, of 3.3 keV to 30 keV (potassium to iodine) are detectable with LiF(200). To have each one of the set peaks in the pulse height spectrum always appear in the same place (= identical pulse height), the electronic amplification must be linked to the goniometer's angle setting. This is achieved by making the main amplifier's amplification factor V for the appropriate crystal (2d value) and the selected reflection order (n) dependent on the sine of the adjustment angle:

$$V \sim \sin \theta$$

This is the only way of ensuring that a discriminator window once set for a crystal will be applicable for all detectable energies (element peaks).

A main amplifier coupled in this way is called a sine amplifier.

Dead Time Correction

The electronics need a certain amount of time to process a pulse during which no other pulse can be registered. This period is called counter channel **dead time** for an individual pulse. As the pulse formation is different for the flow counter and the scintillation counter, the dead times (ca. 300 to 400 ns) are also different for both detectors. The total dead time is the result of an individual pulse multiplied by the pulse rate. As the measured pulses occur statistically distributed over time, the proportion of pulses occurring during the processing period of a previously registered pulse depends on the intensity of the radiation, i.e. the total dead time increases due to the increase of the intensity. This results in a non-linear rise of the measured intensity with the intensity irradiated in the detector. The greater the incident intensity, the greater are the losses during measurement. Fig. 31 illustrates how the dead time is dependent on the increasing incident intensity (increasing generator current). The curve flattens out distinctly at high measured intensities.

A correction of the measured intensities is necessary to produce a linear relationship between incident and measured intensities. A **dead time correction** can be made in the analysis computer. Fig. 31

shows the dead time corrected measurement points. A useful correction can be obtained in tandem operation up to incident intensity of approx. 1.200 kCps per detector. Greater intensities are not worthwhile.

For routine operation it is recommended not to exceed an intensity of approx. 400 KCps per detector.

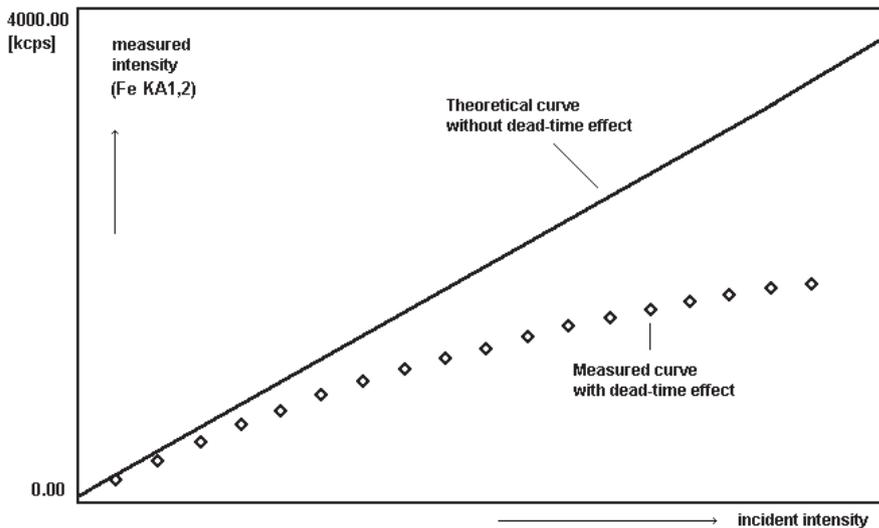


Fig. 30: The dead time effect.

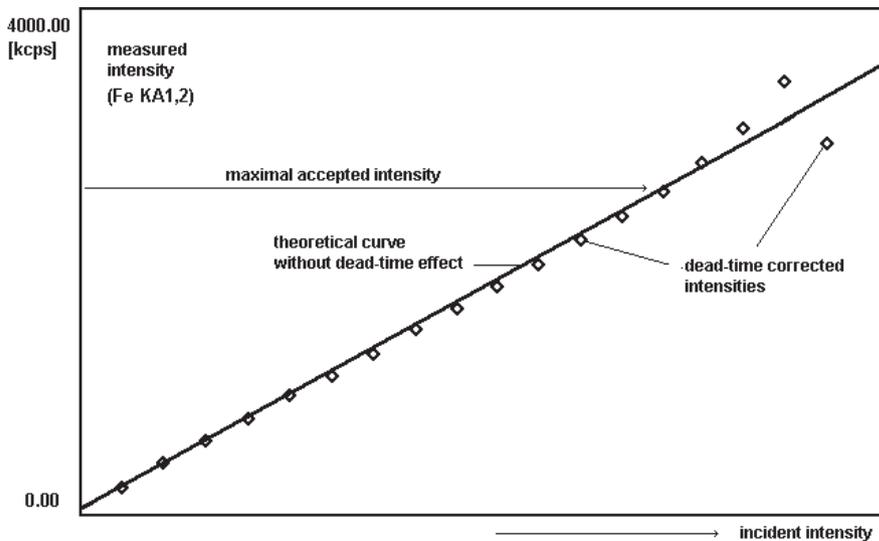


Fig. 31: Dead time corrected readings.

Line-shift Correction

Line-shift correction is only important for the flow counter and the proportional counter at high intensities. It makes itself noticeable when the peak in the pulse height spectrum shifts to lower values at high counting rates. The reason for this is that high counting rates in the detector volume between the flow counter's cathode and counting wire build up a space charge that causes a temporary reduction of the effective high voltage and thus the reduction of gas amplification.

This shift of pulse heights to lower values is automatically corrected by the electronics. The correction can be switched on and off in the software (SPECTRA^{plus}).

Energy Dispersive XRF with the S2 PUMA



Fig. 32: EDXRF spectrometer S2 PUMA

The S2 PUMA uses a 50 W X-ray tube to directly excite the X-ray fluorescence in a sample. By specifying the high voltage and choosing a filter, an elemental or energy range is selected. In order to analyze lighter elements, the sample chamber is either evacuated by means of an integrated vacuum pump or it is flooded with helium. The XFlash detector recognizes the X-ray fluorescence radiation from the sample. The multi-channel analyzer divides up the different energies and accumulates counts to form an intensity vs. energy spectrum.

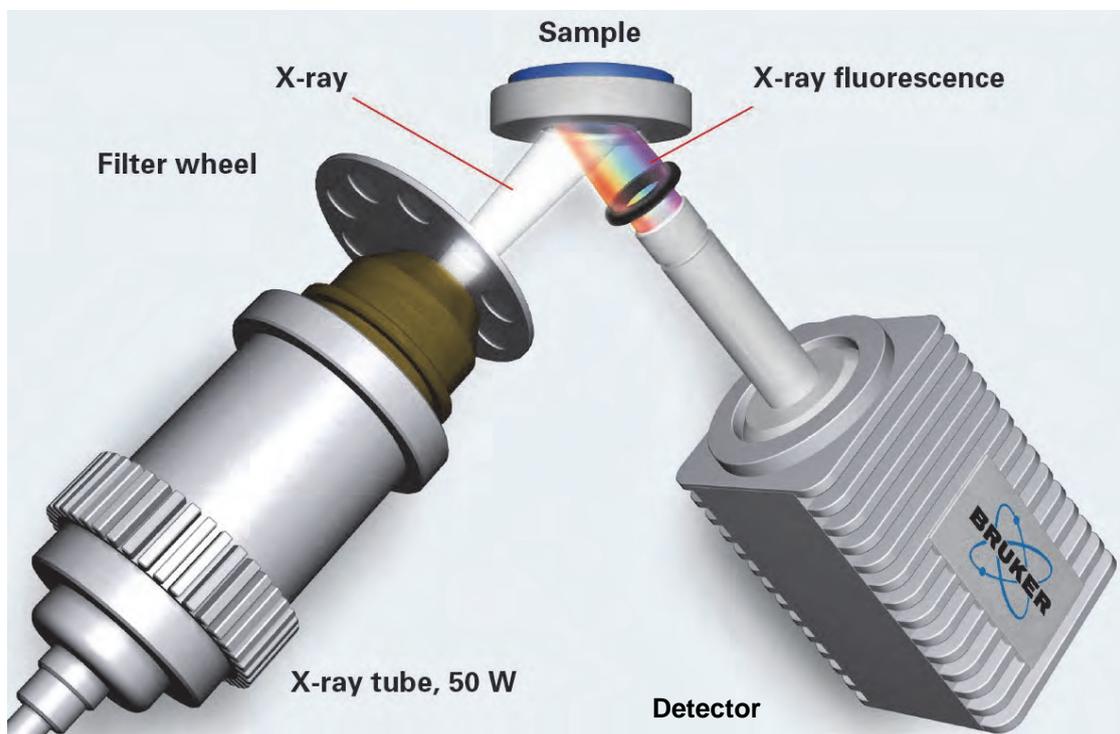


Fig. 33: Beam path in the S2 PUMA.

Basic Principles of the SDD Detectors

The S2 PUMA employs a Silicon Drift Detector (SDD) for the measurement and energy analysis of emitted X-rays. The main advantage of this detector is that it can operate at or close to room temperature with reasonable resolution. At $-25\text{ }^{\circ}\text{C}$ a typical detector has a resolution of less than 129 eV for Mn K- α (5895 eV). By comparison a Si(Li) detector needs to be operated at liquid nitrogen temperature $-196\text{ }^{\circ}\text{C}$ to give a similar performance. A second advantage of the SDD is the high count rate performance of the detector. The time needed to collect the charge generated by the absorption of an X-ray is short compared to Si(Li) and PIN diode detectors. This means that the detector can operate at higher count rates with only a modest increase in measurement dead time. The detector comprises a $450\text{ }\mu\text{m}$ thin piece of Silicon. It is housed in a metal can which is filled with nitrogen gas at 1 atm pressure. The X-rays travel to the chip through an $8\text{ }\mu\text{m}$ Be window and the 1 mm nitrogen gap. The detector is equipped with a specifically coated vacuum tight polymer window for enhanced light element transmission, meaning better transition and less absorption of low energy X-ray photons.

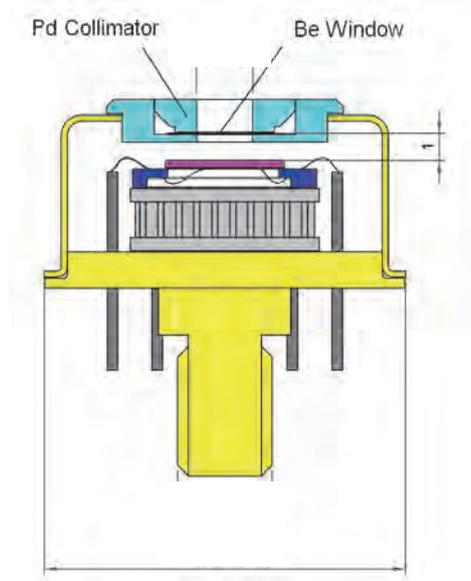


Fig. 34: Schematic cross-section of the detector.

The efficiency of the detector at registering X-rays varies as a function of the X-ray energy. This variation is shown in the figure below.

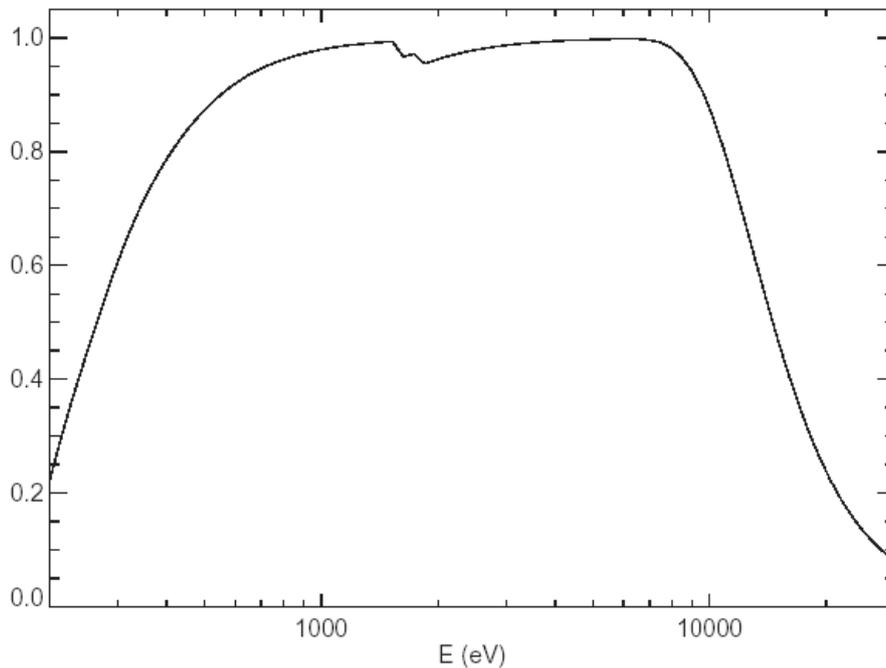


Fig. 35: Quantum Efficiency as a function of photon energy.

The detector chip is most efficient at X-ray energies between 1 and 10 keV. The efficiency of the detector is also dependant on the transmission of X-rays through the detector window and the 1 mm of dry nitrogen in the detector housing.

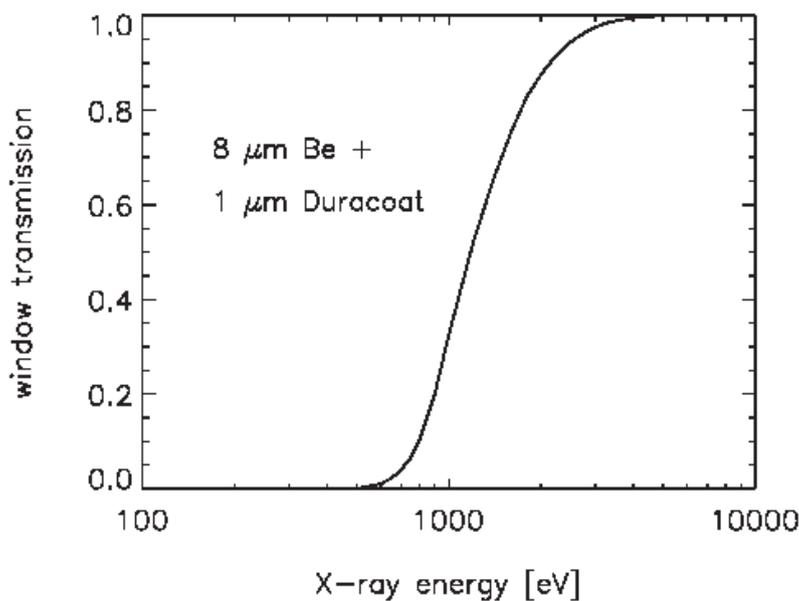


Fig. 36: Transmission of X-rays through 8 μm Dura-Beryllium window.

This means that overall the detector has the maximum sensitivity for energies between 2 kV and 10 kV. Outside these limits the performance drops off rapidly. At the low energies this is due to the window and the nitrogen filling. At the high end, the sensitivity is reduced because of the limited thickness of the detector which means that some X-rays pass through the material without being absorbed. In practical terms this means that the detector with a standard Be window is able to measure the K lines of elements from Na (1.041 keV) to Ba (32.188 keV). A thinner window can be employed to improve the sensitivity of the light elements, but nothing can be done to improve the detection of heavy elements within the drift chamber design.

Energy Resolution

The energy resolution for EDXRF detectors is usually quoted as the full width at half maximum (FWHM) for Mn K- α (5895 eV) X-rays from an Fe-55 source. The energy resolution is the most important parameter on the stability and also the overall performance of the S2 PUMA and therefore some of the influences on the energy resolution will be discussed in detail.

The energy resolution of the detector is a function of the energy of the peaks being measured. The resolution for Al, Mn and Cu are very different for various reasons. The first is that the $K\alpha_1$ and $K\alpha_2$ splitting increases with atomic number. This splitting broadens the width of the peak even in the absence of other effects.

The detector of the S2 PUMA is cooled using an internal Peltier device which has its hot side kept close to room temperature by an additional Peltier device. The detector has the best possible resolution at a temperature of -30 °C. Unfortunately, there are always differences between the single detector chips. Therefore we use temperatures between -25 °C and -5 °C to ensure the same performance for all detectors. The used temperature always ensures that each single detector gets the same energy resolution of ca. 129 eV for Mn K- α (5895 eV) measured at 50 kcps. We can achieve these temperatures up to an ambient temperature (inside of the S2 PUMA) up to 45 °C. Above this the detector temperature may rise causing both a loss of resolution and also possible peak shifts. This is why it is essential to maintain an adequate air flow through the S2 PUMA and make sure that the internal air temperature is between 15 and 40 °C.

Spectral Artefacts in EDXRF

The simplicity of the spectra obtained in XRF is a major advantage compared with other atomic spectroscopy methods. However, there are still peaks in the EDXRF spectrum that arise from sources other than the elements in the sample. For this reason it is important to recognise these features and know how to either avoid them or remove them if they are likely to cause problems. For a more complete discussion of this topic see chapter 3 of handbook of X-ray Spectrometry (item 3 in recommended reading). All spectra will contain a background due to Bremsstrahlung radiation, and if the tube voltage is high enough, Compton and Raleigh scatter peaks which arise from the interaction of the exciting radiation with the sample. The artefacts that remain are discussed briefly below.

Escape Peaks

If an X-ray with an energy greater than the Si-K absorption edge (1.838 keV), is collected by the detector, there is a probability that the detector material will produce its own fluorescent Si $K\alpha$ X-ray. If this X-ray is produced close to the surface of the detector bulk, it is possible for this X-ray to escape before being reabsorbed by the detector. This means that the measured energy will be reduced by 1.740 keV, which is the energy of the escaped Si $K\alpha$ X-ray. The highest probability (~ 3 %) of creating escape peaks occurs just above the absorption edge and falls rapidly with energy (0.1 % @ 10keV). This means that the most critical elements where escape peak can occur are P to Zn. However, for the S2 PUMA this is reduced to the elements Ar to Zn, because the escape peaks of P,S and Cl fall below the low energy cut off (800 eV) of the detector. It must also be remembered that in this range the escape peaks of major elements may be larger than the characteristic lines of trace elements, meaning that the LLD's of the traces will be affected.

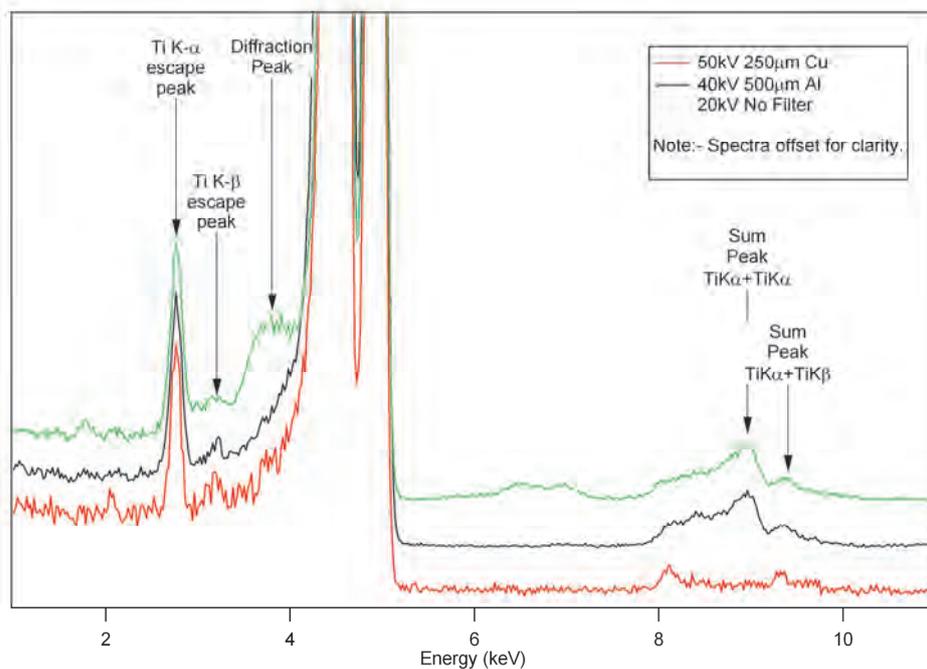


Fig. 37: Spectra from a pure Ti foil measured using a variety of measuring conditions. The various artefacts are indicated.

Sum Peaks

Sum peaks occur when two (or more) X-rays arrive at the detector so close together that the processing electronics is unable to recognise them as separate events. The pulse processing system then sees an X-ray with an energy corresponding to the sum of the combined pulses. The intensity of these sum peaks is dependant on the count rate. For systems with high concentrations of two or more

elements it is possible to get a very complicated set of sum peaks arising from combinations of pulses from different peaks!

Diffraction Peaks

If the sample being measured contains any crystalline material, there is a possibility that the conditions for Bragg diffraction will be met. In the S2 PUMA the geometry has been chosen to reduce this effect, but because of the divergent nature of the incident and scattered beam, there are always positions which will satisfy the condition. The largest diffraction peaks occur when the exiting radiation is not modified by a primary filter, because there is a continuum of energies and angles which can coincide to satisfy the Bragg condition. In the S2 PUMA, excitation energies below 10 keV could give rise to diffraction peaks. In samples where the crystalline planes are aligned, rotating the sample through 90°, or tilting the sample can reduce the effect. However, a much better technique is to use a primary beam filter to remove the primary radiation which is being diffracted. At the same time increasing the tube kV, to shift the energy distribution of the Bremsstrahlung, also helps. In the example above, the Ti diffraction peak is removed by using a filter.

System Contamination Peaks

The S2 PUMA has been designed to minimise the contamination of the spectrum by X-rays emitted from the sample chamber or the sample holder. However, there are still some components which contribute peaks to the spectrum, because they lie directly in the beam path. The main contributions come from the detector collimator, which consists of two components of the same material. The first is a palladium (Pd) collimator which is close to the detector chip, and the second is another palladium (Pd) collimator which is used to select the area of the sample that the detector actually “sees”. If the energies of X-rays hitting the detector are above the Pd L absorption edge, there is a chance of producing Pd secondary X-rays. There is usually also a small amount (<1 %) of Cu K α radiation emitted from the tube which can lead to a small Cu peak in the final spectrum, especially if the sample matrix is composed of low Z material.

Appendix A

Supplementary Literature

Books

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L.S.Birks	X-Ray Spectrochemical Analysis Interscience Publishers, New York Second Edition 1969
Blokhin	Methods of X-Ray Spectroscopic Research Pergamon, New York, 1965
Victor E. Burke, Ron Jenkins, Deane K. Smith (Eds.)	A practical guide for preparation of specimens for X-ray fluorescence and X-ray diffraction analysis Wiley-VCH, 1998, 333 pp. ISBN 0-471-19458-1
Harry Bennet, Graham J. Oliver	XRF Analysis of Ceramics, Minerals and allied materials John Wiley & Sons, 1992 ISBN 0-471-93457-7
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Ron Jenkins	An Introduction to X-Ray Spectrometry Heyden, London - New York - Rheine, 1974
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England

Appendix B

Sources of Standard Samples

NBS	U.S Department of Commerce National Bureau of Standards Washington, DC 20234, USA Tel. : (301) 921-2045
BAS	Bureau of Analyzed Samples Ltd. Newham Hall, Newsby Middlesbrough, Cleveland, TS8 9EA England
CANMET	Canadian Certified Reference Materials 555 Booth Street Ottawa, Ontario, K1A 0G1 Canada
MBH	MBH Analytical Ltd. Certified Reference Materials Holland House, Queens Road, Barnet, Herts EN5 4DJ England
BNF	Analytical Reference Materials Grove Laboratories Denchworth Road Wantage, Oxon, OX12 9BJ England
IRMM	European Commission Directorate-General Joint Research Centre Institute for Reference Materials and Measurements Reference Materials Unit Attn. reference materials sales Retieseweg 111 B-2440 Geel Belgium
ALCOA	Spectrochemical Standards for Analysis of Aluminium and its Alloys Aluminium Company of America Alcoa Laboratories Alcoa Center, Pennsylvania 15069 USA
ALCOA	European sales: Alcoa of Great Britain Ltd. Droitwich, Worcestershire, P.O.Box 15 England
Breitländer LGC Standards	Eichproben und Labormaterial GmbH Mercatorstr.51 D-46485 Wese

Fluxana	Borschelstr.3 47551 Bedburg-Hau Tel. : 02821-997320
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