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Physical and Chemical Analyses of Materials

Chemical analysis: spectrometry

Introduction

⇨ Considered spectrometers are dedicated to the detection of X-rays or electrons (photo- and Auger electrons).

⇨ To provide a chemical analysis, the spectrometer must be qualitative and quantitative.

⇨ Qualification relates to the determination of the chemical nature of the constituting elements and quantification provides the amount of a given chemical element of a material.

X-Ray spectrometers

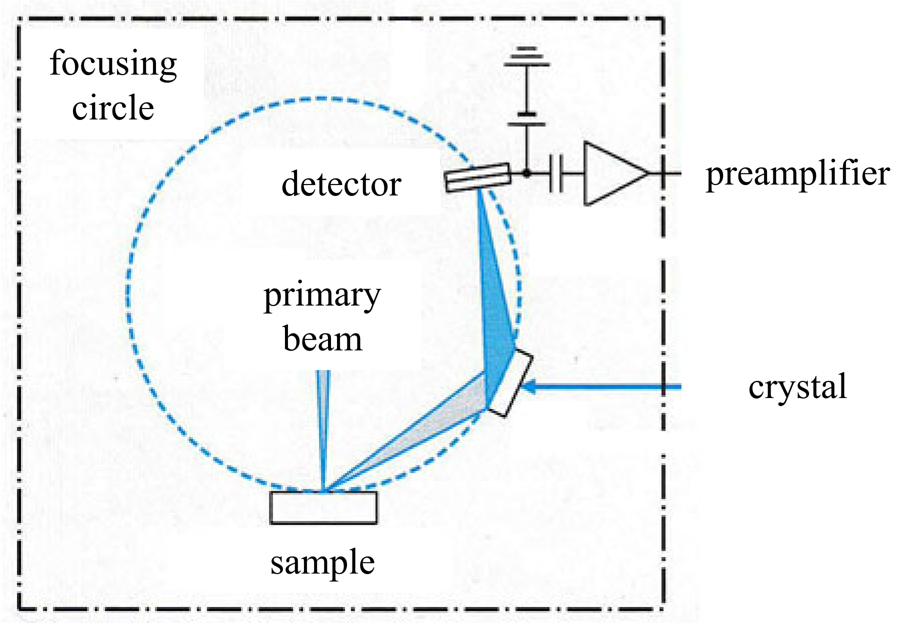
⇨ X-Ray spectrometers include wavelength dispersive and energy dispersive spectrometers, WDS and EDS respectively.

⇨ A WDS spectrometer is constituted by a analyser made of a crystal and a detector. The analyser provides the qualitative information and the detector gives rise to the quantitative one.

⇨ An EDS spectrometer is only constituted by a detector which both provides the qualitative and the quantitative information.

WDS spectrometers

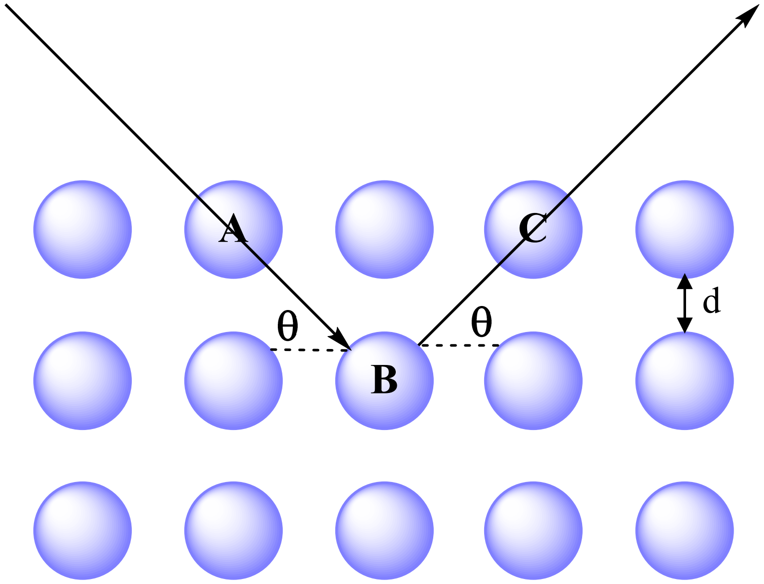
⇨ A WDS spectrometer is made as follows:



⇨ The principal device of the spectrometer is the monochromator constituted by a "perfect" crystal.

⇨ The role of the crystal is to filtrate the polychromatic X-Ray beam emitted by the sample to extract the characteristic emission of a given chemical element.

⇨ The operation of the monochromator is based on the diffraction of the emitted X-Rays by a series of crystallographic planes:



➥ For an interplanar spacing **d**, and an incoming beam angle **θ**, only the rays of wavelength **λ** are scattered to the detector according to the Bragg's law:

$$\mathbf{n\lambda = 2d\sin\theta}$$

➥ For a single diffraction **n** = **1**. When **n** > **1**, it corresponds to multiple diffractions.

➥ The Bragg's law gives a direct correlation between the angle of the emitted X-Ray and its wavelength.

➥ It allows, through the analysis of the emitted wavelengths, to figure out the chemical nature of the components of a material.

⇨ The following table gathers the principal crystals used as monochromators and their key features:

crystal	**Formula (hkl)**	**2d (nm)**	**analysis domain**		
			K lines	**L lines**	**M lines**
LiF	LiF (220)	0.28476	Cr - Pd	Pm - U	-
LiF	LiF (200)	0.40267	Sr - Sc	Te - U	-
Quartz	SiO_2 $(10\bar{1}1)$	0.66862	S - Zn	Mo - Re	Tl - U
PET	$C_5H_{12}O_4$ (002)	0.874	Si - Fe	Sr - Ho	W - U
Mica	$K_2Al_6Si_6O_{20}(F, OH)_4$ (002)	1.984	Ne - Ar	Co - Ag	La - Th
KAP*	$C_8H_5O_4K$ $(10\bar{1}1)$	2.6632	F - P	Mn - Mo	La - Hg
TAP*	$C_8H_5O_4Tl$ $(10\bar{1}1)$	2.575	F- P	Mn - Mo	La - Hg

KAP: Potassium Phtalate Acid, TAP: Thallium Phtalate Acid

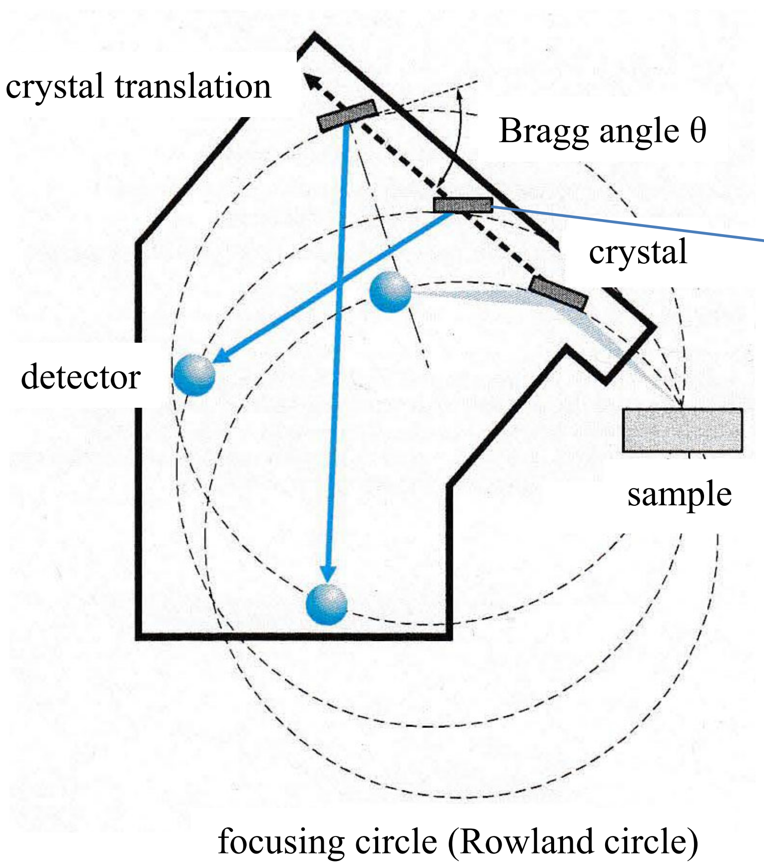
⇨ According to the previous table, it is not possible to analyse the elements lighter than Fluorine. To overcome this limit, some pseudo-crystals made of metallic multilayers are used:

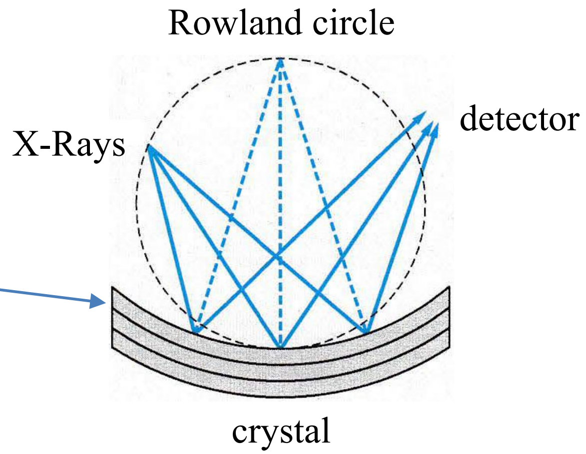
crystal	Formula	2d (nm)	analysis domain		
			K lines	L lines	M lines
ODPb	$(C_{18}H_{35}O_2)_2Pb$	10.0	B - O	Z < V	-
MML	W / Si	4.5	N - F	Z > As	-
MML	W / Si	5.98	C - F	Z < Zn	-
MML	Ni / C	9.5	B - O	Z < Mn	-
MML	Mo / B_4C	14.98	Be - B	-	-

ODPb: Lead Octodecanoate, MML: Metallic MultiLayers

⇨ The WDS spectrometer operates as follows:

↳ The angle of the X-Rays emerging from the crystal is constant whatever the Bragg angle **θ**. The crystal displaces linearly and continuously rotates to modify the incidence angle of the X-rays emitted by the sample:





↳ The crystal is bended with a curvature radius equal to the diameter of the Rowland circle.

↳ The detector follows the crystal displacement on the focusing circle.

↳ The crystal tilt allows the determination of the Bragg angle of a given X-ray so its wavelength and indeed the chemical nature of the emitting element.

↳ Each angle gives rise to a specific X-Ray line. The detector counts the number of photon at each angle and makes the overall sum to provide the percentage of each element present in the material.

↳ The detector is an Ar-CH_4 gas detector working in the proportional domain.

EDS spectrometers

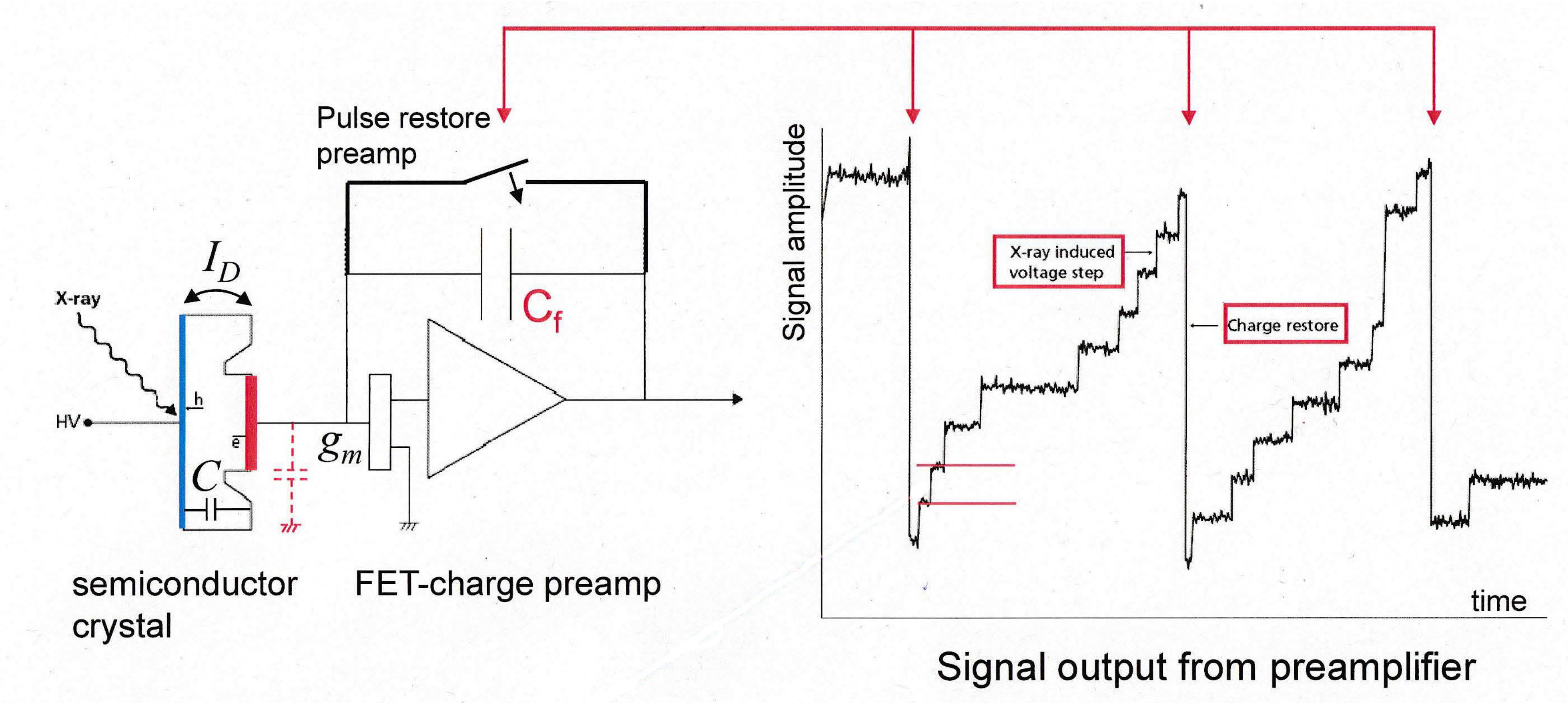
⇨ EDS spectrometers are based on the qualification and the quantification of X-Rays using the detector only.

⇨ In contrast with WDS, a signal treatment allows to obtain both information without the need of a specific analyser.

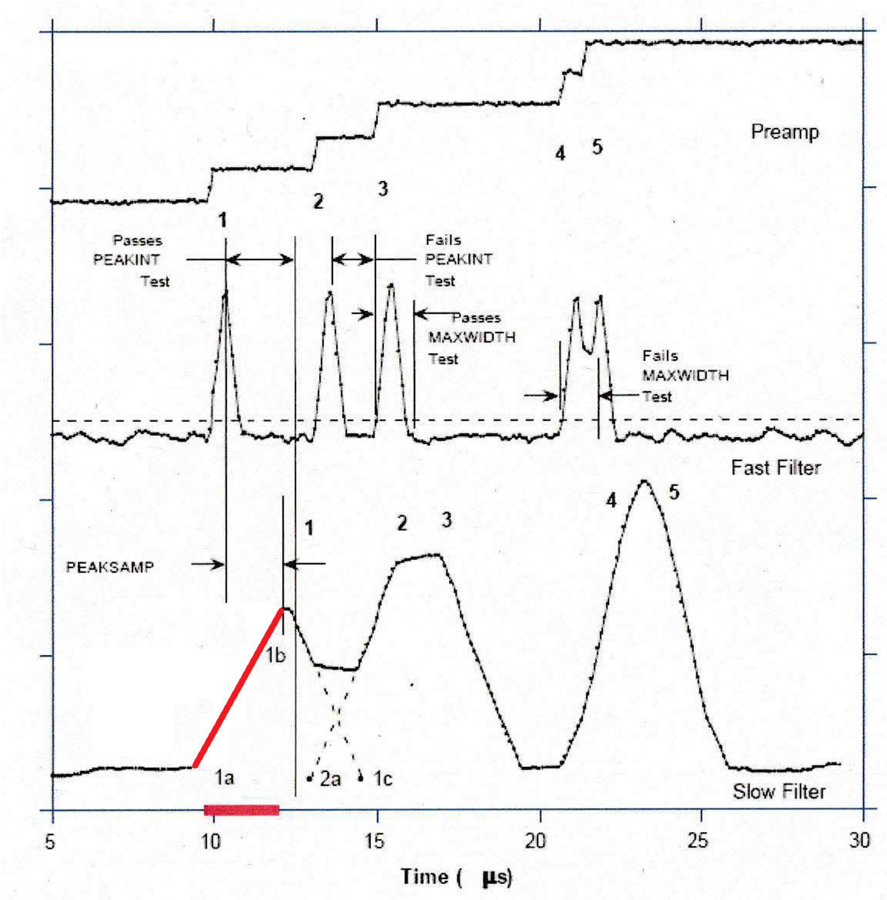
⇨ The detector is usually an Si(Li) or a Ge based detector. Whereas Boron is detected, the lighter element which can be precisely quantified is Carbon.

⇨ When an X-Rays photon interacts with the semiconductor device, its generates a current impulsion, the height of which is proportional to the photon energy.

- The impulsion is integrated over time leading to a charge which is further transformed into an output tension by an electronic chain (preamp feedback capacitance).
- It results into an X-Ray induced voltage step.



- The signal is further derivated and filtered which allows the rejection of pulse pile-up events:



- The peak is considered as a trapeze, the plateau length gives the number of photons and the plateau height provides the energy of the photons. Similar peaks are stored in a same memory address until the end of the recording.

- At the end of the recording, each memory address is associated to a chemical element (energy). The number of stored impulsions (counts per second or counts) in each memory address gives the elemental composition of the material.

- The signal is further converted to a spectrum: number of counts per seconds or number of counts as a function of the energy.

Electron spectrometers

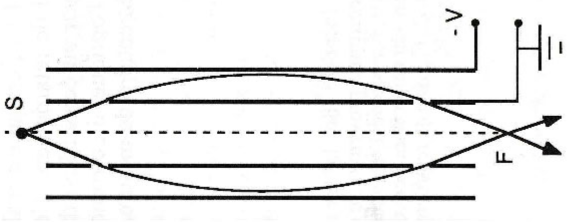
⇨ Electron spectrometers are with or without angular dispersion. The principle is to provide the electrons energy spectrum: counts per seconds or counts as a function of the energy.

Angular dispersion spectrometers

⇨ These spectrometers are the most common ones. They are based on the deviation of the electrons by an electric or a magnetic field. Their relative resolution in energy is about 1%. They provide the qualitative information. They are coupled to an electron detector which gives the quantitative information about the studied material.

Dispersion by an electric field

⇨ These spectrometers can be made of a cylindrical capacitor, *i.e.* cylindrical mirror analyser CMA:

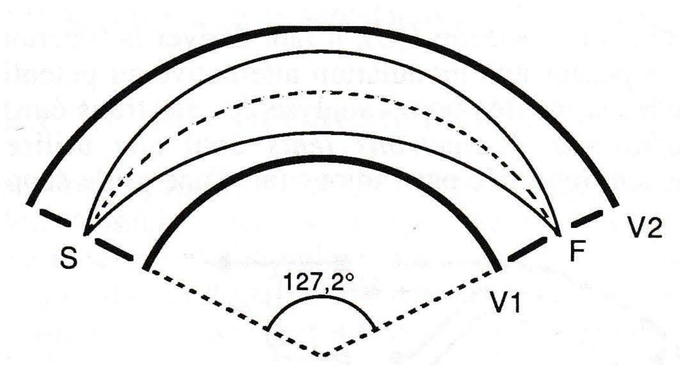


⇳ The applied tension **V** selects some electrons of defined energy **E** emitted from the source **S**.

⇳ These electrons are focused on point **F** and are further detected. The electrons of energy different from **E** are absorbed by the electrodes of the capacitor.

↳ Changing **V** allows to build the electrons energy spectrum.

⇨ These spectrometers can be made of an electrostatic prism, *i.e.* concentric hemispherical analyser CHA:



↳ The electrons emitted from the source **S** follow a circular trajectory of radius **r** in the electric field $\vec{\mathbf{E}}$ if their energy **E** is:

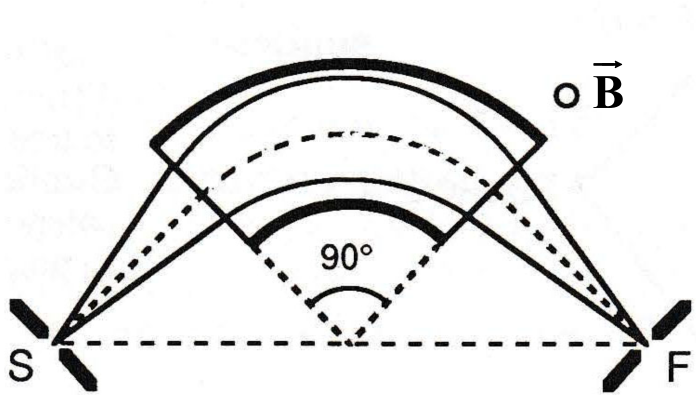
$$\mathbf{E} = 2\mathbf{e}\left\|\vec{\mathbf{E}}\right\|\mathbf{r}$$

↳ The electrons of energy **E** are detected at **F** the others are not selected.

↳ Changing the electric field strength provides the electrons energy spectrum.

Dispersion by a magnetic field

⇨ These spectrometers are built on the same design than the ones made of an electrostatic prism, applying a magnetic field perpendicular to the trajectory of the electrons:



- The electrons emitted from the source **S** follow a circular trajectory of radius **r** in the magnetic field $\vec{\mathbf{B}}$ if their energy **E** is:

$$\mathbf{E} = \frac{\mathbf{e}^2 \left(\left\|\vec{\mathbf{B}}\right\|\right)^2 \mathbf{r}^2}{\mathbf{2m}}$$

- The electrons of energy **E** are detected at **F** the others are not selected.

- Changing the magnetic field strength provides the electrons energy spectrum.

Spectrometers without angular dispersion

- These spectrometers use only the detector to obtain the electrons energy spectrum as for X-Ray energy dispersive spectrometers.

Quantification

Chemical composition of a material

⇨ The chemical composition of a material can be expressed either in relative massic concentration $\mathbf{C_{rm,i}}$ or in relative atomic concentration $\mathbf{C_{ra,i}}$ of a given element **i**:

$$\mathbf{C_{rm,i}} = \frac{\mathbf{C_{m,i}}}{\sum_{\mathbf{i}} \mathbf{C_{m,i}}} \quad \text{and} \quad \mathbf{C_{ra,i}} = \frac{\mathbf{C_{a,i}}}{\sum_{\mathbf{i}} \mathbf{C_{a,i}}}$$

⇨ $\mathbf{C_{m,i}}$ and $\mathbf{C_{a,i}}$ represent the massic and the atomic concentrations of the element **i**.

⇨ The number of atoms $\mathbf{N_{V(i)}}$ of a given element **i** per volume unit (cm^3) is:

$$\mathbf{N_{V(i)}} = \frac{\mathbf{N_A}}{\mathbf{M_i}} \mathbf{C_{rm,i}} \rho$$

⇨ $\mathbf{N_A}$ represents the Avogadro number (6,022×10^{23} mol^{-1}), $\mathbf{M_i}$ is the molar mass (g·mol^{-1}) of the considered element **i**, $\mathbf{C_{rm,i}}$ is the relative massic concentration (dimensionless) of the considered element **i** and $\boldsymbol{\rho}$ (g·cm^{-3}) is the voluminal mass of the material.

⇨ The total number of atoms $\mathbf{N_V}$ per volume unit (cm^3) is: $\mathbf{N_V} = \sum_{\mathbf{i}} \mathbf{N_{V(i)}}$

⇨ The number of atoms $\mathbf{N_{S(i)}}$ of a given element **i** per surface unit (cm^2) is:

$$N_{S(i)} = \frac{N_A}{M_i} C_{rm,i} \rho d$$

↳ $\mathbf{N_A}$ represents the Avogadro number ($6{,}022 \times 10^{23}$ mol^{-1}), $\mathbf{M_i}$ is the molar mass (g·mol^{-1}) of the considered element **i**, $\mathbf{C_{rm,i}}$ is the relative massic concentration (dimensionless) of the considered element **i**, **ρ** (g·cm^{-3}) is the voluminal mass and **d** is the thickness of the material (cm).

⇨ For a material of average molar mass **M** (g·mol^{-1}), $\mathbf{C_{rm,i}}$ and $\mathbf{C_{ra,i}}$ are linked as:

$$C_{ra,i} = \frac{N_{V(i)}}{N_V} = \frac{N_{V(i)}}{\frac{N_A \rho}{M}} = \frac{M}{M_{(i)}} C_{rm,i}$$

Elementary quantitative analysis

Matrix effects

⇨ For the quantitative analysis of a given element **i**, one has to measure its characteristic intensity per volume unit $\mathbf{I_{V(i)}}$.

⇨ its characteristic intensity per volume unit $\mathbf{I}_{\mathbf{V(i)}}$, is linked to the primary beam intensity per atom $\mathbf{I}_{\mathbf{0(a)}}$, the number of atom **i** per volume unit $\mathbf{N}_{\mathbf{V(i)}}$ and the total cross-section $\boldsymbol{\sigma}_{\mathbf{t,i}}$ for the element **i** as:

$$\mathbf{I}_{V(i)} = \mathbf{I}_{0(a)}\mathbf{N}_{V(i)}\boldsymbol{\sigma}_{t,i}$$

↳ The total cross-section $\boldsymbol{\sigma}_{\mathbf{t,i}}$ for the element **i** can be either the excitation (XPS) or the emission (XRFS, XRMA, AES) total cross-section.

⇨ The characteristic intensity per volume unit $\mathbf{I}_{\mathbf{V(i)}}$ of a given element **i** can be affected by the surrounding elements. These effects are called the matrix effects and are described by a constant $\mathbf{K}_{\mathbf{m}}$.

↳ The matrix effects can result in the decrease of the $\mathbf{I}_{\mathbf{V(i)}}$ of the element **i**. The decrease can be due to the quenching of the primary beam and/or the quenching of the emission of the element **i** by the matrix ($\mathbf{K}_{\mathbf{m}} < \mathbf{1}$).

↳ In some cases, the $\mathbf{I}_{\mathbf{V(i)}}$ can be reinforced by the matrix. This can be due to the relaxation of the matrix when excited by the primary beam that will further enhance the excitation of the target element ($\mathbf{K}_{\mathbf{m}} > \mathbf{1}$).

↳ The corrected characteristic intensity per volume unit $\mathbf{I}_{\mathbf{v(i)}}$ is: $\mathbf{I}_{V(i)} = \mathbf{I}_{0(a)}\mathbf{N}_{V(i)}\mathbf{K}_{m}\boldsymbol{\sigma}_{t,i}$

Instrument factors

⇨ The outcoming beam which characterises the elements of the material is translated by the detector according to its transmission factor.

⇨ For an element **i**, its transmission factor $\boldsymbol{\tau}_i$ for a detection solid angle $\boldsymbol{\Omega}$ depends on the detector efficiency $\boldsymbol{\varepsilon}_i$ against the element **i** as: $\boldsymbol{\tau}_i = \boldsymbol{\varepsilon}_i\boldsymbol{\Omega} / 4\boldsymbol{\pi}$.

Measured intensities

⇨ The outcoming beam spectrum displays the measured beam intensity as a function of its energy. The beam intensity is expressed in counts per second or in counts.

⇨ The concentration of an element **i** is measured by the intensity / intensities of its characteristic peak / peaks.

↳ Intensity measured per volume unit: $\mathbf{I}_{V(i)} = \mathbf{I}_{0(a)}\mathbf{N}_{V(i)}\mathbf{K}_m\boldsymbol{\sigma}_{t,i}\boldsymbol{\tau}_i$

↳ Intensity measured per surface unit: $\mathbf{I}_{S(i)} = \mathbf{I}_{0(a)}\mathbf{N}_{S(i)}\mathbf{K}_m\boldsymbol{\sigma}_{t,i}\boldsymbol{\tau}_i$

⇨ As it is not really easy to determine the primary beam intensity per atom $\mathbf{I_{0(a)}}$, one can introduce the primary intensity $\mathbf{I_0}$ shone on the material constituted by $\mathbf{N_v}$ atoms per volume unit when interacting with a defined volume of matter **V**:

$$\mathbf{I_0 = I_{0(a)} N_V \rho V}$$

⇨ For a material of average molar mass **M**, the measured intensity $\mathbf{I_i}$ ($\mathbf{I_i = I_{v(i)} V}$) reads:

$$\mathbf{I_i = I_0 \frac{M}{M_i} C_{rm,i} K_m \sigma_{t,i} \tau_i} \quad \text{or} \quad \mathbf{I_i = I_0 C_{ra,i} K_m \sigma_{t,i} \tau_i}$$

Calibration

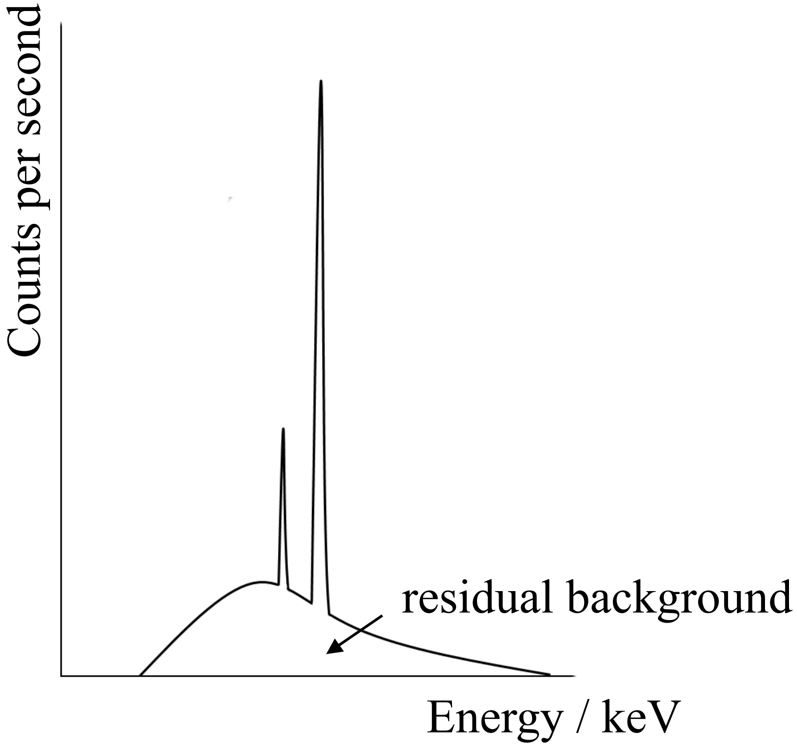
Energy calibration

⇨ The spectrometer is usually calibrated in energy with pure standards. The emission spectra of these standards are measured and the emission lines are attributed and stored.

Concentration calibration

General features

⇨ The spectrometer gives a spectrum which displays a number of counts per second or a number of counts as a function of the energy of the outcoming beam corresponding to the emission of each chemical element present in the material:



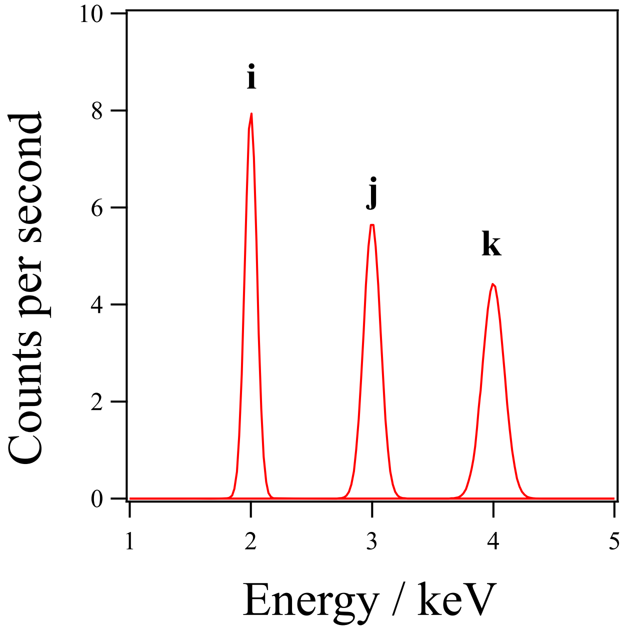
⇨ The spectrum corresponds to a series of peaks. The intensity of a peak is equal to its number of counts per second or its number of counts.

⇨ The measured intensity $\mathbf{I_i}$ of a given chemical element **i** is obtained after background subtraction and is proportional to its massic or atomic relative concentration and to its massic or atomic percentage.

$$\mathbf{\%_{m,i} = 100 \times C_{rm,i}} \quad \text{and} \quad \mathbf{\%_{a,i} = 100 \times C_{ra,i}}$$

Internal standardisation

⇨ Below is considered a spectrum resulting from the subtraction of the background noise:



⇨ The massic percentage or atomic percentage of the element **i** is related to its peak intensity $\mathbf{I_i}$ as:

$$\%_{m,i} = 100\frac{I_i}{\sum I} \quad \text{or} \quad \%_{a,i} = 100\frac{I_i}{\sum I}$$

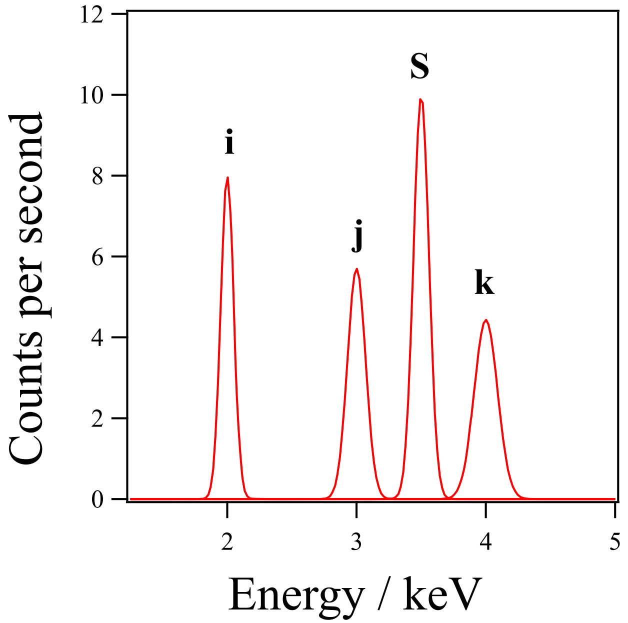
⇨ If matrix effects have to be considered for a given element **i**, then its massic or atomic percentage must be corrected by a given factor.

⇨ The correction factor depends on the analytical method and will be discussed in the concerned chapters.

Internal calibration

⇨ This calibration method is based on the deposition on the material of a given mass of an element **S** which is not present in the analysed material. The element **S** is called an internal standard. The signal of **S** must not be overlapped with the signals of the other elements.

⇨ Below is considered a spectrum resulting from the subtraction of the background noise:



⇨ The resolution between **j** and **S** and between **S** and **k** must be greater than 1.5.

↳ Considering peaks **j** and **S** of energy $\mathbf{E_j}$ and $\mathbf{E_S}$ and with the bases $\mathbf{W_j}$ and $\mathbf{W_S}$, the resolution $\mathbf{R_{s(j,S)}}$ reads:

$$\mathbf{R_{s(j,S)}} = \frac{\mathbf{2(E_S - E_j)}}{\mathbf{W_j + W_S}} \geq \mathbf{1.5}$$

↳ The same consideration must be applied to $\mathbf{R_{s(S,k)}}$.

⇨ The massic percentage or atomic percentage of the element **i** related to its peak intensity $\mathbf{I_i}$ is given by:

$$\frac{\%_{m,i}}{\%_{m,S}} = \frac{I_i}{I_S} \quad \text{or} \quad \frac{\%_{a,i}}{\%_{a,S}} = \frac{I_i}{I_S}$$

⇨ To provide a good precision, the internal standard and the element to evaluate must provide a rather similar behaviour, the atomic numbers of which must be very close.

⇨ If the probed element **i** is affected by matrix effects, then its massic or atomic percentage must be corrected by a given factor.

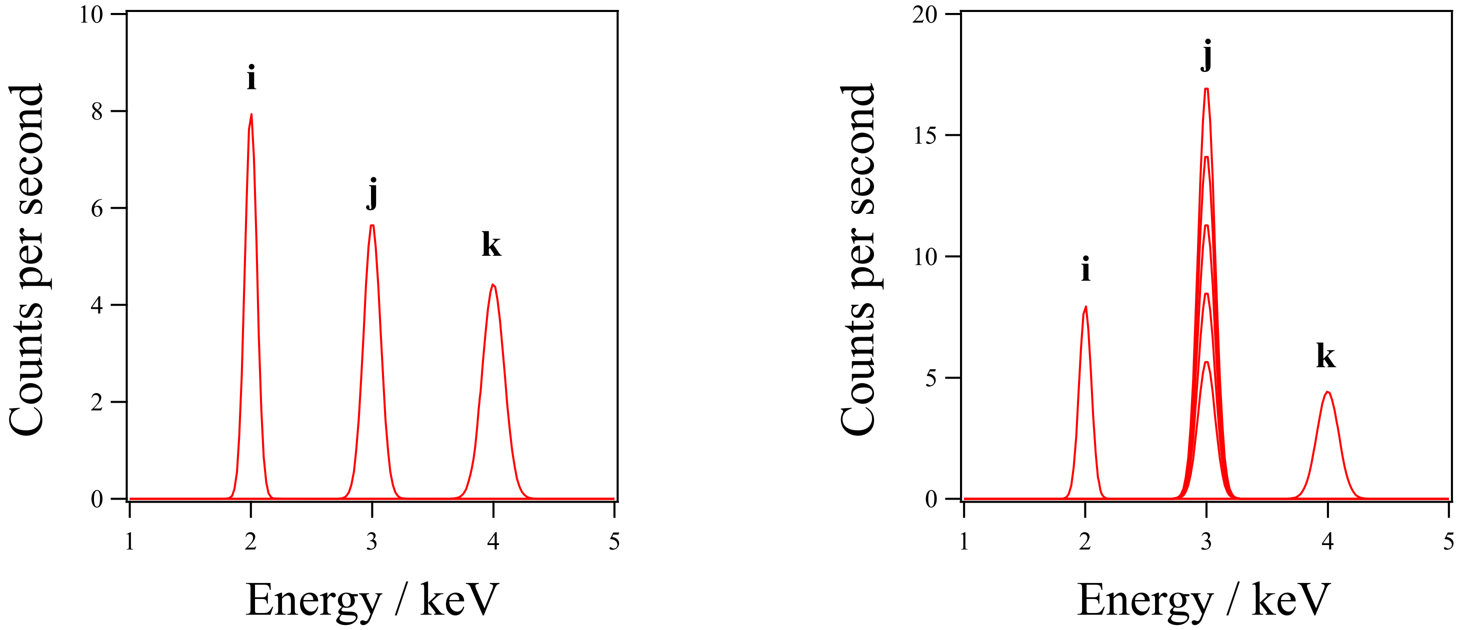
⇨ The correction factor depends on the analytical method and will be discussed in the concerned chapters.

⇨ For specific analytical methods, the chemical nature of primary beam (e.g. monochromatic X-Rays) can be used as internal standard. In this case, a specific line resulting from the elastic scattering of the primary beam will be considered. This concept will be further explored in a chapter dedicated to the concerned methods.

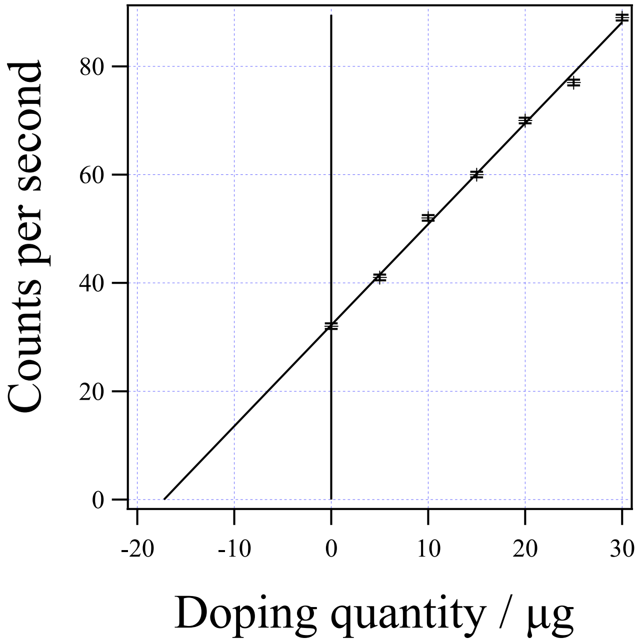
Standard additions

⇨ One of a possible calibration remains into the doping of the material by the element that one wants to quantify. In general, the doping is realised by mass addition.

⇨ Below are considered a spectrum resulting from the subtraction of the background noise (left side) and the evolution of this spectrum as a function of the doping level (right side):



⇨ An example of mass doping of element **j** is given below:



↳ In this case, the doping procedure is linear and the amount of element **j** present in the material is obtained for $\mathbf{I}_\mathbf{j} = 0$.

↳ The obtained value being negative one has to consider the absolute value of the determination.

↳ As the doping of the material is realised with the same element that one would like to quantify, there is no further matrix effects to consider.

↳ This is only true if the amount of added dopant does not disturb the absorption of the primary beam by the element to be quantified.