

Lectures about XRF (X-Ray Fluorescence)

Advanced Physics Laboratory
Laurea Magistrale in Fisica

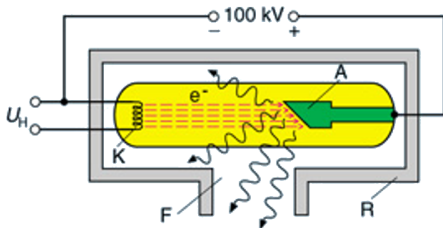
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X-ray Fluorescence

- **XRF** is an acronym for 'X-Ray Fluorescence'.
- The XRF technique is considered one of the most widespread and useful methods for the determination of presence and quantity of the elements in a given substance.
- X-ray fluorescence is a consequence of the ionization of atoms, for which the excited state returns to the ground state emitting x-ray photons of well-defined energies.
- The characteristic x-ray emission can be induced either by interaction with charged particles or with x-ray photons generated by a Coolidge tube.
- The XRF technique here discussed is based on the primary excitation of a x-ray beam, followed by the secondary x-ray fluorescence emission. The x-ray emission is then detected and analysed by a photon detector, usually a solid state device characterized by a sufficient energy resolution.

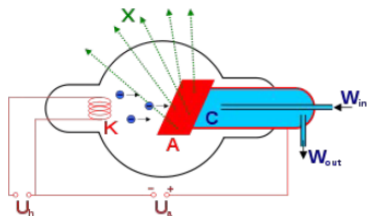
X-ray Fluorescence

- As an example, a typical tube used as a x-ray generator (known as *Coolidge tube*) is described in the following figure:



- There are of course many alternative ways of producing x-rays: rotating anodes, radioisotopes (Fe^{55} , Cd^{109} , Am^{241}), storage rings.

This device was designed by William Coolidge in 1913. The Coolidge tube, also called hot cathode tube, is the most widely used. It works with a good quality vacuum (about 10^{-4} Pa, or 10^{-9} Atm). In the Coolidge tube, the electrons are produced by thermionic effect from a tungsten filament heated by an electric current. The filament is the cathode of the tube. The high voltage potential is between the cathode and the anode, the electrons are thus accelerated, and then hit the anode.



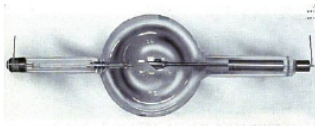
Coolidge side-window tube (scheme)

K: filament

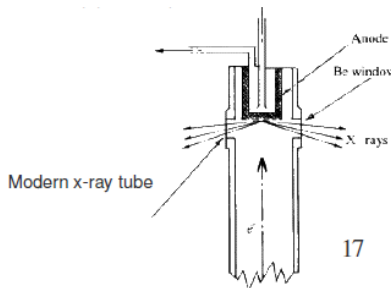
A: anode

W_{in} and W_{out}: water inlet and outlet of the cooling device (C)

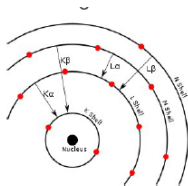
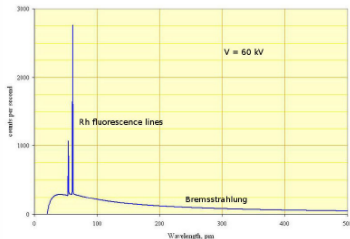
Usually in this (sidewindow) tubes we find an Electrostatic Lens to focus the beam onto a very small spot on the anode. The anode is specially designed to dissipate the heat and wear resulting from this intense focused barrage of electrons: Mechanically spun to increase the area heated by the beam. Cooled by circulating coolant. The anode is angled at 120 degrees off perpendicular to the electron current so as to allow escape of some of the X-ray photons which are emitted essentially perpendicular to the direction of the electron current. The anode is usually made out of W, Mo, or Cu. The tube has a window designed for escape of the generated Xray photons. The power of a Coolidge tube usually ranges from 1 to 4 kW.



Coolidge X-ray tube, from around 1917. The heated cathode is on the left, and the anode is on the right. The X-rays are emitted downwards.



The x-ray emission spectrum at the anode consists basically in two components: the Bremsstrahlung (deceleration) radiation and the x-ray fluorescence pattern. The first is a continuous spectrum extending up to the limiting electron energy (for example 20 keV if the potential difference between the anode and the cathode is 20 kV). The x-ray fluorescent pattern is instead composed by well-defined peaks located at energy (or wavelengths) typical of the atomic constituents of the anode. These energies reflect the electronic structure of the atoms. The origin of the Bremsstrahlung is due to the deceleration imposed to the electrons arriving inside the anode from the surface, while the x-ray fluorescence pattern is due to the emission of photons as a result of a de-excitation of the electrons of the atomic core levels (originally excited as a result of the “collisions” with the electrons of the incoming beam).



X-ray Fluorescence: the x-ray source

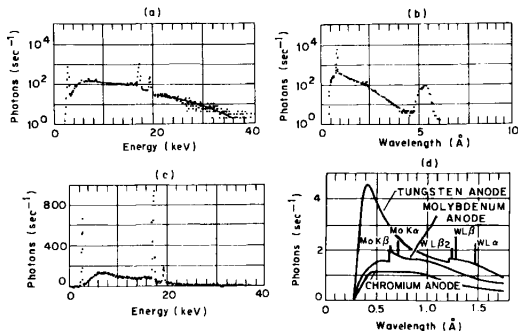


Figure 3.1 Spectra from thick anode x-ray tubes. (a) The energy spectrum from a molybdenum anode x-ray tube measured with a Si(Li) detector (40 kV tube voltage, 39- μm -thick beryllium x-ray tube window, 90° electron beam incidence angle, 32° x-ray takeoff angle). Although the low spectral intensity near 40 keV makes accurate measurement of E_{max} difficult, the spectrum approaches zero intensity near 40 keV. The Mo K lines occur at 17.4 keV and 19.8 keV, and the L lines are visible at 2.4 keV. (b) The spectrum from (a) transformed into the wavelength coordinate system. The Mo L line at 5.3 Å is broad due to the Si(Li) detector energy resolution. The value of λ_{min} is readily apparent at 0.31 Å. (c) The spectrum from (a) on a linear vertical scale. (d) Spectra from tungsten, molybdenum, and chromium anode x-ray tubes. The positions of characteristic lines are marked by vertical lines of arbitrary height. (Adapted from R. Tertian, *Fluorescence X, Theorie et Pratique de l'Analyse*, Thesis, Université de Paris, and reprinted by courtesy of EG&G ORTEC.)

X-ray Fluorescence

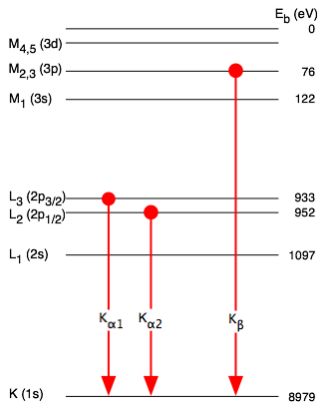
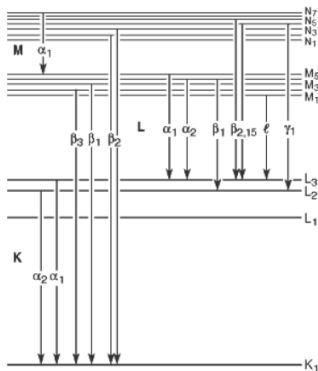
- XRF is a non-invasive technique, leaving the sample unchanged after application. In fact, the electrons involved in the x-ray emission processes are those related to the core levels and for this reason chemical bonds, structure and morphology are not affected. Moreover, the number of excitation processes is low as compared to the available electrons (weak field approximation, valid for all of the x-ray sources except free-electron lasers). A notable exception for the application of XRF is on bio-materials, for which changes can be observed.
- The samples do not usually need any specific preparation because the energy of the exciting photons is usually high enough (10-30 keV) allowing us to analyse depths of the order of 10 microns or more.

X-ray Fluorescence

- The examination of the XRF spectra allows us to identify the atomic species present in a given sample. In fact, the energy of the x-ray emission lines is a well-defined function of the atomic number Z (see following slides).
- For its powerful information content and simple application methodology, the XRF technique is applied in many different contexts and fields, from basic physics to chemistry, material science and mineralogy.

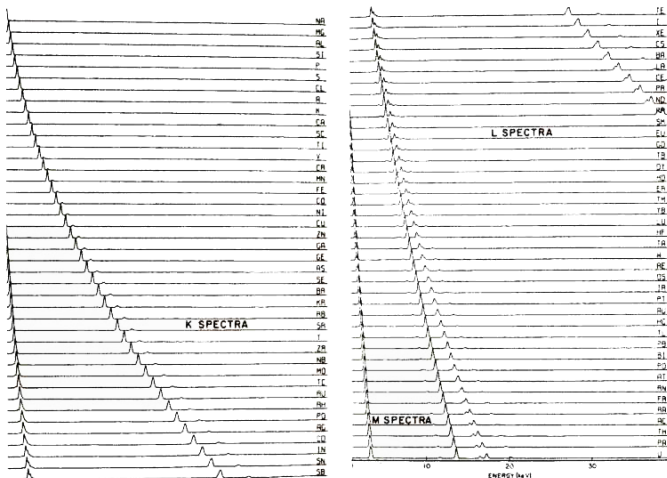
X-ray Fluorescence

- Atomic levels involved in the emission of x-ray emission according to the accepted terminology (line K_{α_1} corresponds to a transition from the L_3 ($2p_{3/2}$) to the K ($1s$) level).



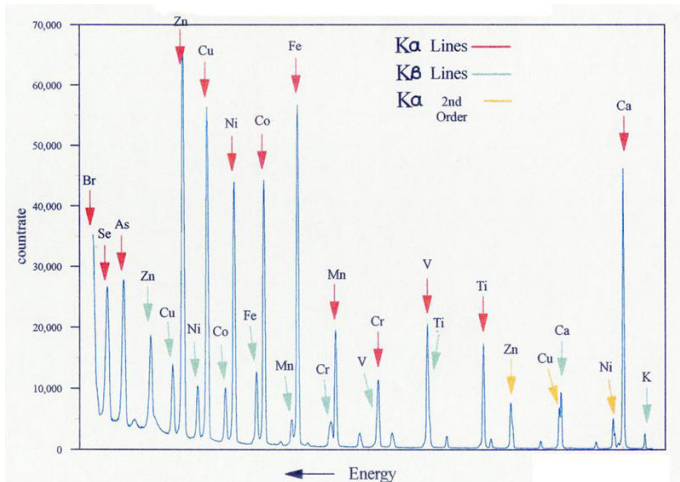
X-ray Fluorescence

- X-ray emission spectra (K, L, M) ordered according to the atomic number of the elements.



X-ray Fluorescence

- Typical Fluorescence pattern obtained using an energy-dispersive detector.



X-ray Fluorescence

- For light (Mg, Al, Si, Ca ..) or medium-Z (Cr, Fe, Cu, Ag ..) elements the x-ray emission lines of the K series are used preferentially (those involving the $1s$ core electrons).
- For heavier elements (like Au, Pb ..) the L emission lines, falling in the useful x-ray range under investigation, are used. Those lines involved transitions to the upper levels $2s$, $2p_{3/2}$, $2p_{1/2}$.
- There are different methods for collecting XRF spectra depending on the particular experimental needs, basically divided into energy and angular dispersive techniques.

X-ray Fluorescence

- The XRF collected in *Wavelength Dispersive* mode (WDX, or WDAX, or WDS) the spectrum of emitted photons is measured after a monochromator (crystal). This method is based on a complex experimental set-up and usually requires longer collection times but can give an excellent energy resolution.
- The rapid collection of x-ray emission patterns is allowed by the use of modern solid-state detectors coupled with standard multi-channel electronics for photon counting. Those detectors can have sufficient energy resolution to identify different emission lines and are at the basis of the energy dispersive spectrometry (EDS, EDX or *Energy Dispersive Analysis X-EDAX*). The experimental set-up may be portable.

X-ray Fluorescence

- Typical XRF set-up using broadband x-ray sources.

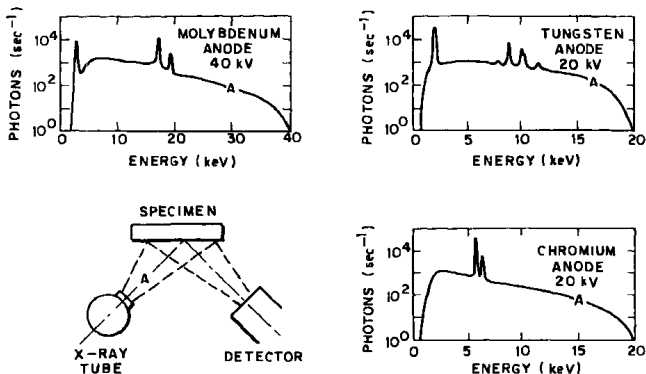


Figure 3.7 The geometry used for broadband excitation. The spectra depict several commonly used anode materials; the vertical scale is logarithmic. (Reprinted by courtesy of EG&G ORTEC.)

X-ray Fluorescence: detectors

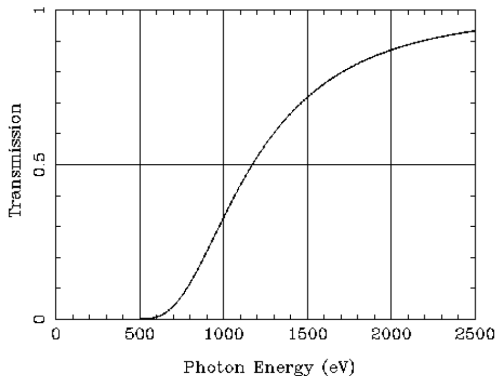
- There are several limitations of the solid-state detectors including their resolution and energy-dependent efficiency, which is also limited for low energies by the Be window protecting the detector (light elements can not be detected).
- The *Be* window is used for two main reasons:
 1. Protection of the solid-state (Si or Ge typically)
 2. Preservation of the internal vacuum conditions, in which the sensor is cooled down (using liquid nitrogen or thermoelectric devices) avoiding condensation of water onto the detector.

X-ray Fluorescence: detectors

- Transmission of a *Be* window (thickness of 10 μm)

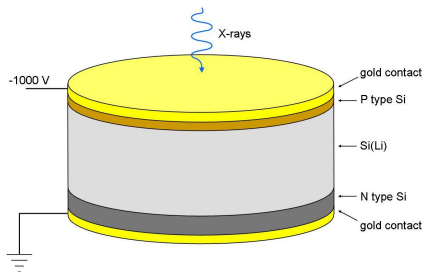
Filter Transmission

Be Density=1.848 Thickness=10. microns



X-ray Fluorescence: detectors

Good solid-state detectors consist essentially of a 300-500 microns thick silicon junction type p-i-n diode (PIN) with a bias up to 1000 V across it. The lithium-drifted centre part forms the non-conducting i-layer, where Li compensates the residual acceptors which would otherwise make the layer p-type. When an X-ray photon passes through, it causes a swarm of electron-hole pairs to form, and this causes a voltage pulse. To obtain sufficiently low conductivity, the detector must be maintained at low temperature, and liquid-nitrogen must be used for the best resolution. With some loss of resolution, the much more convenient Peltier cooling can be employed.



X-ray Fluorescence: detectors

Ordinary Silicon PIN photodiodes can serve as detectors for X-ray and gamma ray photons. The detection efficiency is a function of the thickness of the silicon wafer. For a wafer thickness of 300 microns (ignoring attenuation in the diode window and/or package) the detection efficiency can be close to 100% at 10 KeV, falling to approximately 1% at 150 KeV(3). For energies above approximately 60 KeV, photons interact almost entirely through Compton scattering. Moreover, the active region of the diode is in electronic equilibrium with the surrounding medium—the diode package, substrate, window and outer coating, etc., so that Compton recoil electrons which are produced near—and close enough to penetrate—the active volume of the diode, are also detected. For this reason the overall detection efficiency at 150 KeV and above is maintained fairly constant (approximately 1%) over a wide range of photon energies. A silicon PIN diode can be thought of as a solid-state equivalent to an ionization-chamber radiation detector.



X-ray Fluorescence: detectors



145 eV Resolution!

All solid state design...

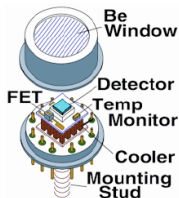
No more liquid nitrogen!

XR-100 Landed on Mars!



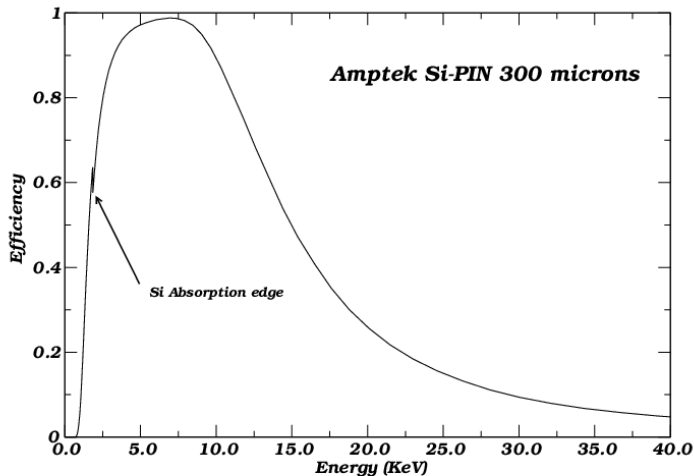
The XR-100CR is a high performance x-ray detector, preamplifier, and cooler system using a thermoelectrically cooled Si-PIN photodiode as an x-ray detector. Also mounted on the 2-stage cooler are the input FET and a novel feedback circuit. These components are kept at approximately $-55\text{ }^{\circ}\text{C}$, and are monitored by an internal temperature sensor. The hermetic TO-8 package of the detector has a light tight, vacuum tight thin Beryllium window to enable soft x-ray detection.

The XR-100CR represents a breakthrough in x-ray detector technology by providing "off-the-shelf" performance previously available only from expensive cryogenically cooled systems.



X-ray Fluorescence: detectors

Knowledge of the photon collection yield of the detector is important for a quantitative analysis of the XRF spectra.



X-ray Fluorescence

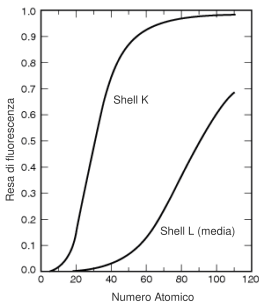
- An important feature of the XRF is the possibility of performing a chemical analysis in a rapid and non-destructive way.
- In particular this technique allows us:
 - a) **Qualitative analysis** for the identification of the elements through the position of the typical x-ray emission lines in the XRF spectra.
 - b) **Quantitative analysis** that needs an accurate data-analysis accounting for the intensity of the different x-ray emission lines. The measured intensity depends in fact on a number of factors including the characteristic of the source, of the detector, of the geometry, and sample morphology. The use of standards with known concentration of the elements under investigation is particularly important for precise determinations.

X-ray Fluorescence

- Qualitative analysis, limited to the identification of the atomic species, is relatively simple.
- Nevertheless, in some cases there is an almost perfect overlap of emission lines of two successive series (L e K, M ed L, . . .) hindering the identification of some elements.
- In those cases, a better energy resolution of the detector (obtained for example using an angular dispersive technique) may be necessary.
- When the emission lines are overlapped and/or the concentration of one of the elements is very low, the identification of the presence of a selected atomic species may be not possible and further inspections may be needed.

X-ray Fluorescence

- *Fluorescence yield* for K and L levels.



- The excited states (ionization of core electrons) created by the interaction with the primary photons (or by other processes) are followed by a recombination process following different routes (schematically divided into radiative and non-radiative processes). The *Fluorescence yield* indicates the fraction of de-excitation processes involving the emission of fluorescence photons.

Fluorescence yield references

A Review, Bibliography, and Tabulation of K , L , and Higher Atomic Shell X-Ray Fluorescence Yields

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The measured K , L , and higher atomic shell x-ray fluorescence yield data, covering the period 1978 to 1993, following the major previous compilations by Bambynek *et al.* (1972) and Krause (1979), are reviewed. An annotated bibliography of x-ray fluorescence yield measurements, analyses, fits and tables 1978–1993 is presented. Comparisons of the fluorescence yields ω_K , ω_L , and ω_{HL} based on measurements, and on theoretical models, are presented. Values of ω_K , ω_L , and ω_{HL} fitted to standard empirical parametric formulations, are presented. In addition, selected well-characterized measured ω_K , ω_L , and ω_{HL} results restricted to the period 1978–1993 are listed. These selected measured values are fitted by least squares to polynomials in Z of the form $\sum_{i=0}^n a_i Z^i$ and compared with theoretical and with earlier fitted values. A section on application of fluorescence yield data to computations of x-ray energy-absorption coefficients is included.

330

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X-Ray Fluorescence Yields, Auger, and Coster-Kronig Transition Probabilities*

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*The present status of the field of fluorescence yields, radiationless (Auger and Coster-Kronig) and radiative transition probabilities is summarized. Tables of experimental and theoretical results are included, and tables of "best values" of important quantities are presented.

The x-ray data booklet

X-RAY DATA BOOKLET

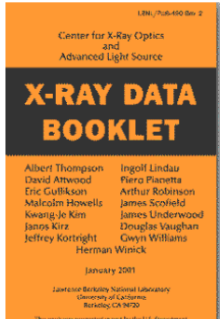
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X-ray Fluorescence: quantitative analysis

- An important feature of the XRF technique is that it is possible, under certain conditions, obtain quantitative information about the concentration of the chemical species present in a given sample (stoichiometry).
- Theoretical background and methods for performing a reliable quantitative analysis are discussed in various textbooks and specialized articles. Here we shall refer our discussion to the book “Quantitative X-ray Spectrometry” by Ron Jenkins, R. W. Gould, and Dale Gedcke (2nd edition, 1995).
- The theoretical framework is fully understood, but the technique is more easily applied to samples with specified thickness and morphology (grain size, texture, surface) and the use of standards of known concentration is often necessary for reliable determinations.
- The application is vast, from mineralogy to material science, from chemistry to metallurgy also using electron microscopy equipments.

XRF - Quantitative analysis: x-ray absorption

For a piece of material of finite thickness x , such as shown in Fig. 2.10(b), integration of Eq. (2.7) shows that the transmitted intensity of photons that have not suffered interactions in the material is given by

$$I(E) = I_0(E)e^{-\mu(E)\rho x} \quad (2.8)$$

This is the Beer-Lambert law. The mass attenuation coefficient $\mu(E)$ accounts for the various interactions that can occur in the specimen. Thus $\mu(E)$ is composed of three major components:

$$\mu(E) = \tau(E) + \sigma_{\text{coh}}(E) + \sigma_{\text{inc}}(E) \quad (2.9)$$

The number of photons per second that interact in the slab is expected to be proportional to both the incident photon rate $I_0(E)$ and the mass per unit area of the slab, which is given by ρdx . This can be stated as

$$-dI(E) = \mu(E) I_0(E) \rho dx \quad (2.7)$$

where the proportionality constant is $\mu(E)$. The constant $\mu(E)$ is called the *mass attenuation coefficient*. It is characteristic of the material in the slab and the energy of the x-ray photons. The units of $\mu(E)$ are square centimeters per gram (cm^2/g) when the density ρ is expressed in grams per cubic centimeter (g/cm^3) and thickness is specified in centimeters (cm).

$\tau(E)$ is the photoelectric mass absorption coefficient, which describes the photoelectric effect. The coherent scattering process is defined by the total coherent mass scattering coefficient $\sigma_{\text{coh}}(E)$, and $\sigma_{\text{inc}}(E)$ is the total incoherent mass scattering coefficient. Both $\sigma_{\text{coh}}(E)$ and $\sigma_{\text{inc}}(E)$ include all possible scattering angles.

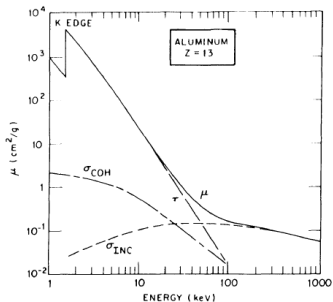


Figure 2.12 Mass attenuation coefficient and its components for aluminum as a function of incident photon energy. (Reprinted by courtesy of EG&G ORTEC.)

XRF: trend of the X-ray absorption cross-section

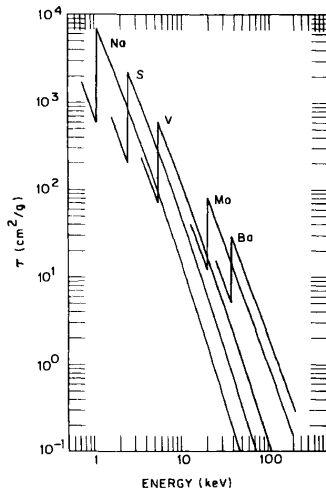


Figure 3.2 The photoelectric mass absorption coefficient for several elements at and above the K absorption edge. (Reprinted by courtesy of EG&G ORTEC.)

XRF - Quantitative analysis: x-ray absorption and geometry

When a material is made up of a homogeneous mixture of pure elements, the resultant mass attenuation coefficient may be calculated from

$$\mu = \sum_j W_j \mu_j \quad (2.11)$$

where μ_j is the mass attenuation coefficient of element j present in the material with a weight fraction W_j . The sum is carried over all elements in the material such that

$$\sum_j W_j = 1 \quad (2.12)$$

These photons strike the surface of the specimen at an incidence angle ψ_1 .

The number of characteristic x-rays fluoresced in the differential element of thickness dx , located a distance x behind the specimen surface, is to be calculated. In order to reach this volume element, the incident x-rays must pass through an effective specimen thickness $x \csc \psi_1$. As a result of absorption along this path length, the rate of photons arriving at the differential volume element is reduced to

$$I_1 = I_0(E_0) dE_0 d\Omega_1 \exp[-\mu(E_0) \rho x \csc \psi_1] \quad (2.13)$$

where $\mu(E_0)$ is the total mass attenuation coefficient in square centimeters per gram

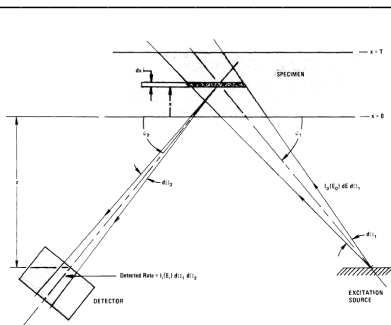


Figure 2.15 Geometry for derivation of the primary fluorescence intensity. (Reprinted by courtesy of EG&G ORTEC.)

XRF - Quant. anal.: excitation of specific (K) core levels

In passing through the differential volume element the x-rays travel through a thickness $dx \csc \psi_1$. Therefore the number of photoelectric interactions in this element per unit time is given by

$$I_2 = I_1 \tau(E_0) \rho dx \csc \psi_1 \quad (2.14)$$

where $\tau(E_0)$ is the total photoelectric mass absorption coefficient of the specimen (cm^2/g). Note that $\tau(E_0)$ is the weighted average of the photoelectric mass absorption coefficients for the elements making up the specimen. That is,

$$\tau(E_0) = \sum_m W_m \tau_m(E_0) \quad (2.15)$$

where W_m is the weight fraction of the m th element in the specimen and $\tau_m(E_0)$ is the total photoelectric mass absorption coefficient of the m th element. The m th term in Eq. (2.15) determines the number of interactions with the m th element. Since it is only the excitation of the i th element that is of interest, the number of photoelectric interactions to be considered is reduced to

$$\begin{aligned} I_3 &= \frac{W_i \tau_i(E_0)}{\tau(E_0)} I_2 \\ &= I_1 W_i \tau_i(E_0) \rho dx \csc \psi_1 \end{aligned} \quad (2.16)$$

Furthermore, the term $\tau_i(E_0)$ accounts for ionization in all the atomic shells of the i th element where the electron-binding energy ϕ is less than the excitation photon energy E_0 . Typically it is only the x-rays caused by electron transitions to *one* of the shells that is monitored in the fluorescence spectrometer. For example, it will be assumed that only the K x-rays of element i are being measured. In this case the number of ionizations of the K shell is reduced to

$$\begin{aligned} I_4 &= \frac{\tau_{Ki}(E_0)}{\tau_i(E_0)} I_3 \\ &= I_1 W_i \tau_{Ki}(E_0) \rho dx \csc \psi_1 \end{aligned} \quad (2.17)$$

where $\tau_{Ki}(E_0)$ is the photoelectric mass absorption coefficient for only the K shell of element i .

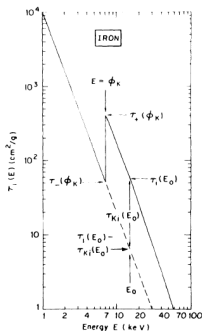


Figure 2.16 Derivation of the approximate value of $\tau_{Ki}(E_0)$. (Reprinted by courtesy of EG&G ORTEC.)

The K edge jump ratio is defined as

$$\Gamma_K = \frac{\tau_+(\phi_K)}{\tau_-(\phi_K)} \quad (2.18)$$

$$\frac{\tau_i(E_0)}{\tau_i(E_0) - \tau_{Ki}(E_0)} \approx \frac{\tau_+(\phi_K)}{\tau_-(\phi_K)} = \Gamma_K \quad (2.19)$$

$$\tau_{Ki}(E_0) \approx \frac{\Gamma_K - 1}{\Gamma_K} \tau_i(E_0)$$

XRF - Quant. anal.: inclusion of specific contributions

Equation (2.17) gives the rate of ionization of the K shell of the i th element. Following ionization, the vacancies in the K shell are filled by electron transitions from other shells with lower binding energies. In some of these transitions Auger electrons are emitted. In the remaining transitions characteristic K x-rays are emitted. The K-shell fluorescence yield ω_K describes the fraction of the K-shell ionizations that are followed by emission of characteristic K-series x-rays. Therefore the rate of emission of K x-rays from the i th element is

$$I_5 = \omega_{K_i} I_4 \quad (2.20)$$

Generally speaking, only one of the lines from the K series will be measured. The energy of the monitored line will be denoted E_i . If this line represents a fraction f of the total photon rate in the entire K series, then the emitted photon rate in the analyzed line is

$$I_6 = f I_5 \quad (2.21)$$

This photon rate is emitted isotropically in all directions, i.e., into a solid angle of 4π steradians. The photon rate emitted toward the detector into the differential solid angle $d\Omega_2$ at a takeoff angle ψ_2 is given by

$$I_7 = \frac{d\Omega_2}{4\pi} I_6 \quad (2.22)$$

Before emerging from the specimen the characteristic x-ray can suffer absorption in the path length $x \csc \psi_2$. This reduces the emitted photon rate to

$$I_8 = I_7 \exp[-\mu(E_i) \rho x \csc \psi_2] \quad (2.23)$$

where $\mu(E_i)$ is the specimen total mass attenuation coefficient for the characteristic x-ray energy E_i . If the detector efficiency for recording a photon of energy E_i is $\eta(E_i)$, then the detected photon rate in the detector is

$$I \, dx \, dE_0 = \eta(E_i) I_8 \quad (2.24)$$

$$\begin{aligned} I_i(E_i) \, d\Omega_1 \, d\Omega_2 &= \int_{E_0=\phi_K}^{E_{\max}} \int_{x=0}^T I \, dx \, dE_0 \\ &= d\Omega_1 \left(\frac{d\Omega_2}{4\pi} \right) \frac{\eta(E_i)}{\sin \psi_1} \int_{E_0=\phi_K}^{E_{\max}} Q_{if}(E_0) \\ &\quad \times \left(\frac{1 - \exp[-\rho T \{\mu(E_0) \csc \psi_1 + \mu(E_i) \csc \psi_2\}]}{\mu(E_0) \csc \psi_1 + \mu(E_i) \csc \psi_2} \right) \\ &\quad \times I_0(E_0) \, dE_0 \end{aligned} \quad (2.25)$$

where $Q_{if}(E_0)$ contains all the fundamental parameters associated with fluorescing the characteristic x-rays from element i .

$$\begin{aligned} Q_{if}(E_0) &= W_i \tau_{K_i}(E_0) \omega_{K_i} f \\ &\approx W_i \tau_i(E_0) \frac{r_K - 1}{r_K} \omega_{K_i} f \end{aligned} \quad (2.26)$$

Note that the integral over the excitation spectrum can be evaluated only if the shape of the excitation spectrum is known.

Neglecting effects of finite size and angle distributions:

$$\begin{aligned} I_i(E_i) &= \frac{\eta(E_i)}{4\pi \sin \psi_1} \int_{E_0=\phi_K}^{E_{\max}} Q_{if}(E_0) \\ &\quad \times \left(\frac{1 - \exp[-\rho T \{\mu(E_0) \csc \psi_1 + \mu(E_i) \csc \psi_2\}]}{\mu(E_0) \csc \psi_1 + \mu(E_i) \csc \psi_2} \right) \\ &\quad \times I_0(E_0) \, dE_0 \end{aligned} \quad (2.27)$$

XRF - Quant. anal.: monochromatic source

- The integral disappears if we can consider the source monochromatic (energy E_0) reducing considerably several problems in the data-analysis.

If the excitation source is monochromatic (emits only one energy), Eq. (2.27) simplifies to

$$I_i(E_i) = \frac{\eta(E_i)}{4\pi \sin \psi_1} Q_{if}(E_0) \times \left(\frac{1 - \exp[-\rho T[\mu(E_0) \csc \psi_1 + \mu(E_i) \csc \psi_2]]}{\mu(E_0) \csc \psi_1 + \mu(E_i) \csc \psi_2} \right) \times I_0(E_0) \quad (2.29)$$

XRF - Quant. anal.: infinite thickness

- If the thickness of the sample can be considered infinite (with respect to the typical photon absorption lengths, the inverse of the absorption coefficient) further simplifications are obtained. Typical absorption lengths in the x-ray range (~ 10 keV) are of the order of $10 \mu\text{m}$.

If the specimen thickness T is infinite, then the exponential term vanishes in both Eq. (2.27) and Eq. (2.29). That is, for infinitely thick specimens the fluoresced intensity is

$$I_i(E_i) = \frac{\eta(E_i)}{4\pi \sin \psi_1} \int_{E_0=\phi_K}^{E_{\max}} \frac{Q_{if}(E_0)I_0(E_0) dE_0}{\mu(E_0) \csc \psi_1 + \mu(E_i) \csc \psi_2} \quad (2.30)$$

or for monochromatic excitation,

$$I_i(E_i) = \frac{\eta(E_i)}{4\pi \sin \psi_1} \frac{Q_{if}(E_0)I_0(E_0)}{\mu(E_0) \csc \psi_1 + \mu(E_i) \csc \psi_2} \quad (2.31)$$

The question arises as to how thick a specimen must be to yield virtually all the fluoresced intensity that would be obtained from an infinitely thick specimen. If 99% of the infinite thickness intensity is adequate, then the exponential term in Eq. (2.25) must have a value of 0.01. This defines the critical thickness as

$$\begin{aligned} T_{99\%} &= \frac{-\ln 0.01}{\rho[\mu(E_0) \csc \psi_1 + \mu(E_i) \csc \psi_2]} \\ &= \frac{-\ln(1 - 0.99)}{\rho[\mu(E_0) \csc \psi_1 + \mu(E_i) \csc \psi_2]} \quad (2.32) \end{aligned}$$

Specimens that are thick compared with $T_{99\%}$ can be considered to be infinitely thick.

XRF - Quant. anal.: secondary absorption

- The actual intensity of the fluorescence lines depends also on the secondary self-absorption of the sample. So quantitative analysis must take account of both primary and secondary absorption terms, acting at different photon energies.

The secondary absorption effect is due to interaction of the characteristic x-ray photons excited within the specimen and all types of atoms making up the specimen. The total secondary absorption $\mu(\lambda_i) \text{csc } \psi_2$ for a given characteristic photon of wavelength λ_i from an analyte element i , is given by Eq. (2.33).

$$\mu(\lambda_i) \text{csc } \psi_2 = \sum_j W_j \mu_j(\lambda_i) \text{csc } \psi_2 \quad (2.33)$$

where W_j is the weight fraction of element j and the index j represents all types of atoms making up the specimen, including the analyte element. For a given absorbing element j , the value of $\mu_j(\lambda_i)$ is a constant characteristic of the analyte wavelength λ_i .

primary and secondary absorption terms.*

$$\alpha_T(\lambda_i) = \sum_j W_j [\mu_j(\lambda_0) \text{csc } \psi_1 + \mu_j(\lambda_i) \text{csc } \psi_2] \quad (2.34)$$

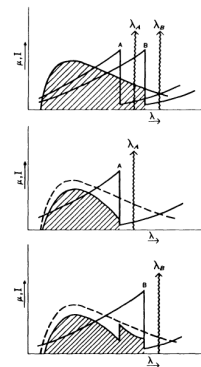


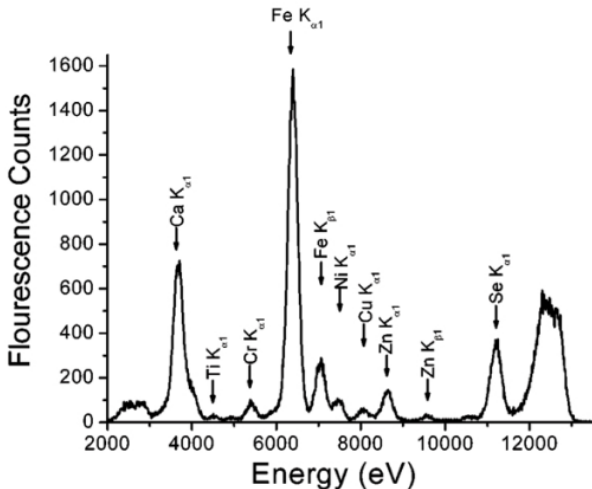
Figure 2.17 Total primary spectrum available for the excitation of elements A and B (the hatched area represents the spectral distribution of photons available for excitation).

XRF: Quantitative analysis

- Quantitative XRF data-analysis is possible within the above-mentioned theoretical framework. Geometry of the experiment, source and detector features must be taken into account.
- Practical data-analysis is based on a peak-fitting technique, in which several fluorescence peaks are identified above a measured background.
- The intensity of each peak is given by the integrated number of counts related to each peak (after background subtraction).
- Concentration (W_i) of element i can be obtained by solving the corresponding set of equations for each observed fluorescence peak.
- Full statistical analysis can be done taking into account the experimental noise.

X-ray Fluorescence

- Typical shape of a XRF spectrum. Peaks indicate the presence of well-defined chemical species.



X-ray Fluorescence

- Typical analysis of XRF spectra: removal of background, peak-fitting parameters.

