Chapter 3. X-ray fluorescence analysis

3.1 Introduction

XRF analysis is a powerful analytical tool for the spectrochemical determination of almost all the elements present in a sample. XRF radiation is induced when photons of sufficiently high energy, emitted from an X-ray source, impinge on a material. These primary X-rays undergo interaction processes with the analyte atoms. High-energy photons induce ionization of inner shell electrons by the photoelectric effect and thus electron vacancies in inner shells (K, L, M, ...) are created. The prompt transition of outer shell electrons into these vacancies within some 100 fs can cause the emission of characteristic fluorescence radiation. Not all transitions from outer shells or subshells are allowed, only those obeying the selection rules for electric dipole radiation. The creation of a vacancy in a particular shell results in a cascade of electron transitions, all correlated with the emission of photons with a well-defined energy corresponding to the difference in energy between the atomic shells involved. The family of characteristic X-rays from each element including all transitions allows the identification of the element. Next to this radiative form of relaxation, a competing process can take place: the emission of Auger electrons. Both processes have Z-dependent probabilities that are complementary: the Auger yield is high for light elements and the fluorescence yield is high for heavy elements.

The working principle of XRF analysis is the measurement of wavelength or energy and intensity of the characteristic X-ray photons emitted from the

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sample. This allows the identification of the elements present in the analyte and the determination of their mass or concentration. All the information for the analysis is stored in the measured spectrum, which is a line spectrum with all characteristic lines superimposed above a certain fluctuating background. Other interaction processes, mainly the elastic and inelastic scattering of the primary radiation on sample and substrate, induce the background.

Measurement of the spectrum of the emitted characteristic fluorescence radiation is performed using wavelength dispersive (WD) and energy dispersive (ED) spectrometers. In wavelength dispersive X-ray fluorescence analysis (WDXRF), the result is an intensity spectrum of the characteristic lines versus wavelength measured with a Bragg single crystal as dispersion medium while counting the photons with a Geiger-Müller, a proportional or scintillation counter. In energy dispersive X-ray fluorescence analysis (EDXRF), a solid-state detector is used to count the photons, simultaneously sorting them according to energy and storing the result in a multichannel memory. The result is an X-ray energy vs. intensity spectrum. The range of detectable elements ranges from Be ($Z = 4$) for the light elements and goes up to U ($Z = 92$) on the high atomic number $Z$ side. The concentrations that can be determined with standard spectrometers of WD or ED type lie are situated in a wide dynamic range: from the percent to the $\mu$g/g level. In terms of mass the nanogram range is reached with spectrometers having the standard excitation geometry.

By introducing special excitation geometries, optimized sources and detectors, the picogram and even femtogram range of absolute analyte detection capacity can be reached; in terms of concentrations, the same improvement factor can be attained, i.e. from the $\mu$g/g towards the pg/g level under the best conditions.
In principle, XRF analysis is a multielement analytical technique and in particular, the simultaneous determination of all the detectable elements present in the sample is inherently possible with EDXRF. In WDXRF both the sequential and the simultaneous detection modes are possible.

The most striking feature of XRF analysis is that this technique allows the qualitative and quantitative analysis of almost all the elements (Be–U) in an unknown sample. The analysis is in principle nondestructive, has high precision and accuracy, has simultaneous multielement capacity, requires only a short irradiation time so that a high sample throughput is possible; online analysis is also possible and the running costs are low. The technique is extremely versatile for applications in many fields of science, research and quality control, has low detection limits, and a large dynamic range of concentrations covering up to 9 orders of magnitude. The physical size of an XRF spectrometer ranges from handheld, battery-operated field units to high-power laboratory units with compact tabletop units and larger ones requiring several cubic meters of space including a 10–20 kW electrical power supply and efficient cooling units with high pressure water and a heat sink.

In contrast to all these attractive properties there are some disadvantages. The absorption effects of the primary radiation and the fluorescence radiation created in the analyte result in a shallow layer a few tenths of a millimeter deep that provides information on its composition. This requires a perfectly homogeneous sample which often occurs naturally but must sometimes be produced by acid dissolution into liquids or by grinding and the preparation of pressed pellets. In both examples the feature of non-destructiveness is lost. Most ideally thin films or small amounts of microcrystalline structure on any substrate are the ideal analyte where also the quantification process is simple because there is linearity between fluorescence intensity and concentration. In thick samples corrections for absorption and enhancement effects are necessary.
While the roots of the method go back to the early part of this century, where electron excitation systems were employed, it is only during the last 30 years or so that the technique has gained major significance as a routine means of elemental analysis.

### 3.2 Basic Principles

#### 3.2.1 X-ray wavelength and energy scales

The X-ray or Röntgen region of the electromagnetic spectrum starts at ca. 10 nm and extends towards the shorter wavelengths. The energies of X-ray photons are of the same order of magnitude as the binding levels of inner-shell electrons (K, L, M, ... levels) and therefore can be used to excite and/or probe these atomic levels. The wavelength $\lambda$ of an X-ray photon is inversely related to its energy $E$ according to:

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

where 1 eV is the kinetic energy of an electron that has been accelerated over a voltage difference of 1 V (1 eV = 1.602 $10^{-19}$ J). Accordingly, the X-ray energy range starts at 100 eV and continues towards higher energies. X-ray analysis methods most commonly employ radiation in the 1-50 keV (1 - 0.02 nm) range.

#### 3.2.2 Interaction of X-rays with matter

When X-ray beam passes through matter, some photons will be absorbed inside the material or scattered away from the original path, as illustrated in Fig. 3.1. The intensity $I_0$ of an X-ray beam passing through a layer of thickness $d$ and density $\rho$ is reduced to an intensity $I$ according to the well-known law of Lambert-Beer:

$$
I = I_0 e^{-\mu \rho d}
$$

(1)
The number of photons (the intensity) is reduced but their energy is generally unchanged. The term $\mu$ is called the mass attenuation coefficient and has the dimension cm$^2$/g. The product $\mu L = \mu \rho$ is called the linear absorption coefficient and is expressed in cm$^{-1}$. $\mu(E)$ is sometimes also called the total cross-section for X-ray absorption at energy $E$.

![Diagram of X-ray photon interaction](image)

**Fig. 3.1.** Interaction of X-ray photons with matter.

Fig. 3.2 shows a log-log plot of the energy dependence of the mass attenuation coefficient of several chemical elements in the X-ray energy range between 1 and 100 keV. The absorption edge discontinuities (due to photoelectric absorption – see below) are clearly visible. Low Z materials attenuate X-rays of a given energy less than high Z materials. A given material will attenuate high energy (i.e. hard) X-rays less than low energy (soft) X-rays.
Fig. 3.2. Energy dependence of the mass absorption coefficient $\mu$ of several elements.

The mass absorption coefficient $\mu(M)$ of a complex matrix $M$ consisting of a mixture of several chemical elements (e.g., an alloy such as brass), can be calculated from the mass attenuation coefficient of the $n$ constituting elements:

$$\mu(M) = \sum_{i=1}^{n} w_i \mu_i$$ (2)

where $\mu_i$ is the mass attenuation coefficient of the $i^{th}$ pure element and $w_i$ its mass fraction in the sample considered. This is called the mixture rule.

The mass absorption coefficient $\mu$ plays a very important role in quantitative XRF analysis. Both the exciting primary radiation and the fluorescence radiation are attenuated in the sample. To relate the observed fluorescence intensity to the concentration, this attenuation must be taken into account.
As illustrated in Fig. 3.1, the absorption of radiation in matter is the cumulative effect of several types of photon-matter interaction processes that take place in parallel. Accordingly, in the X-ray range the mass attenuation coefficient $\mu_i$ of element $i$ can be expressed as:

$$\mu_i = \tau_i + \sigma_i$$  \hspace{1cm} (3)

where $\tau_i$ is the cross-section for photo-electric ionization and $\sigma_i$ the cross-section for scattering interactions. All above-mentioned cross-sections are energy (or wavelength) dependent. Except at absorption edges (see below), $\mu$ is more or less proportional to $Z^4\lambda^3$.

3.2.3 Photo-electric effect

In the photo-electric absorption process (see Fig. 3.3), a photon in completely absorbed by the atom and an (inner shell) electron is ejected. Part of the photon is used to overcome the binding energy of the electron and the rest is transferred in the form of kinetic energy. After the interaction, the atom (actually an ion now) is left in a highly excited state since a vacancy has been created in one of the inner shells. The atom will almost immediately return to a more stable electron configuration by emitting an Auger electron or a characteristic X-ray photon. The latter process is called X-ray fluorescence. The ratio of the number of emitted characteristic X-rays to the total number of inner-shell vacancies in a particular atomic shell that gave rise to it, is called the fluorescence yield of that shell (e.g., $\omega_k$). For light elements ($Z < 20$), predominantly Auger electrons are produced during the relaxation upon K-shell ionisation ($\omega_K < 0.2$) while the medium to heavy elements are preferentially relaxing in a radiative manner ($0.2 < \omega_K < 1.0$).
Photo-electric absorption can only occur if the energy of the photon $E$ is equal or higher than the binding energy $\phi$ of the electron. For example, an X-ray photon with an energy of 15 keV can eject a K-electron ($\phi_K = 7.112$ keV) or an L$_3$-electron ($\phi_{L3} = 0.706$ keV) out of a Fe atom. However, a 5 keV electron can only eject L-shell electrons from such an atom.

Since photo-electric absorption can occur at each of the (excitable) energy levels of the atom, the total photo electric cross section $\tau_1$ is the sum of (sub)shell-specific contributions:
\[ \tau_i = \tau_{i,K} + \tau_{i,L} + \tau_{i,M} + \ldots = \tau_{i,K} + (\tau_{i,L1} + \tau_{i,L2} + \tau_{i,L3}) + (\tau_{i,M1} + \ldots + \tau_{i,M5}) + \ldots \] (4)

In Fig. 3.4, the variation of \( \tau_{Mo} \) with energy is plotted. At high energy, e.g., above 50 keV, the probability for ejecting a K-electron is rather low and that for ejecting an L₃-electron is even lower. As the energy of the X-ray photon decreases, the cross section increases, i.e., more vacancies are created. At the binding energy \( \phi_K = 19.99 \) keV there is an abrupt decrease in the cross-section because X-rays with lower energy can no longer eject electrons from the K-shell. However, these photons continue to interact with the (more weakly bound) electrons in the L and M-shells. The discontinuities in the photo-electric cross-section are called absorption edges. The ratio of the cross section just above and just below the absorption edge is called the jump ratio, \( r \). As X-ray fluorescence is the result of selective absorption of radiation, followed by spontaneous emission, an efficient absorption process is required. An element can therefore be determined with high sensitivity by means of XRF when the exciting radiation has its maximum intensity at an energy just above the K-edge of that element.

Fig. 3.4. Variation of \( \tau_{Mo} \) as a function of X-ray photon energy. The K, L₁, L₂ and L₃ absorption edges are clearly visible.
3.2.4 Scattering

Scattering is the interaction between radiation and matter which causes the photon to change direction. If the energy of the photon is the same before and after scattering, the process is called elastic or Rayleigh scattering. Elastic scattering takes place between photons and bound electrons and forms the basis of X-ray diffraction. If the photon loses some of its energy, the process is called inelastic or Compton scattering.

Accordingly, the total cross section for scattering $\sigma_i$ can be written as the sum of two components:

$$\sigma_i = \sigma_{R,i} + \sigma_{C,i}$$  \hspace{1cm} (5)

where $\sigma_{R,i}$ and $\sigma_{C,i}$ respectively denote the cross sections for Rayleigh and Compton scatter of element $i$.

Compton scattering occurs when X-ray photons interact with weakly bound electrons. After inelastic scattering over an angle $\phi$, a photon (see Fig. 3.5), with initial energy $E$, will have a lower energy $E'$ given by the Compton equation:

$$E' = \frac{E}{1 + \frac{E}{m_0 c^2}(1 - \cos \phi)}$$  \hspace{1cm} (6)

where $m_0$ denotes the electron rest mass.

Fig. 3.5. Geometry for Compton scattering of X-ray photons.
3.2.5 Bremsstrahlung

When an energetic electron beam impinges upon a (high Z) material, X-rays in a broad wavelength band are emitted. This radiation is called Bremsstrahlung as it is released during the sudden deceleration of the primary electrons, as a result of their interaction with the electrons of the lattice atoms in the target. At each collision, the electrons are decelerated and part of the kinetic energy lost is emitted as X-ray photons. (In addition, also characteristic X-ray lines (see below) of the target materials are produced.) Since during one collision, an electron of energy $E$ can lose any amount between zero and $E$, the resulting bremsstrahlung continuum features photons with energies in the same range. On a wavelength scale, the continuum is characterized by a minimal wavelength $\lambda_{\text{min}}$ (nm) = $1.24/E_{\text{max}}$ (keV) = $1.24/V$ (kV) where $E_{\text{max}}$ is the maximum energy of the impinging electrons and $V$ the potential used to accelerate them. The continuum distribution reaches a maximum at 1.5-2 $\lambda_{\text{min}}$ so that an increase in the accelerating potential $V$ causes a shift of the continuum towards shorter wavelengths. In Fig. 3.6 bremsstrahlung spectra emitted by X-ray tubes operated at different accelerating potentials are shown.

![Figure 3.6](image)

Fig. 3.6. Polychromatic excitation spectra emitted by a Rh X-ray tube operated at various accelerating voltages. The excitation spectrum consists of a bremsstrahlung continuum upon which the characteristic lines of the anode material are superimposed.
3.2.6 Selection rules, characteristic lines and X-ray spectra

Characteristic X-ray photons are produced following the ejection of an inner orbital electron from an excited atom, and subsequent transition of atomic orbital electrons from states of high to low energy. Each element present in the specimen will produce a series of characteristic lines making up a polychromatic beam of characteristic and scattered radiation coming from the specimen. The systematic (IUPAC) name of the X-ray line arising from a vacancy in the K-shell of an atom, which is filled by an electron originally belonging to the L3-shell of that atom is the K-L3 transition. However, this transition is more commonly referred to as the Kα-line (non-systematic or Siegbahn nomenclature); similarly, fluorescent X-rays resulting from L3-M5 transitions are better known as Lα1-photons. Table 3.1 lists a number of observed X-ray lines and their corresponding IUPAC Siegbahn names.

Moseley first established the relationship between the wavelength $\lambda$ of a characteristic X-ray photon and the atomic number $Z$ of the excited element (see Fig. 3.7). Moseley’s law is written as:

$$\frac{1}{\lambda} = K(Z - s)^2 \quad (7)$$

where $Z$ is atomic number and $K$ and $s$ are constants. $s$ is the shielding constant and takes a value close to one. $K$ has a different value for each of the line series considered (e.g., the Kα-lines, the Lα-lines – see Table 3.1). Each unique atom has a number of available electrons that can take part in the transfer and, since millions of atoms are typically involved in the excitation of a given specimen, all possible de-excitation routes are taken. These de-excitation routes can be defined by a simple set of selection rules that account for the majority of the observed wavelengths.
Table 3.1. Principal X-ray lines (IUPAC and Siegbahn notations) and their approximate intensities relative to the major line in each subshell.

<table>
<thead>
<tr>
<th>Series</th>
<th>IUPAC name</th>
<th>Siegbahn name</th>
<th>Relative Intensity</th>
</tr>
</thead>
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<tr>
<td>K-lines</td>
<td>K-L₃</td>
<td>Kₐ₁</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>K-L₂</td>
<td>Kₐ₂</td>
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</tr>
<tr>
<td></td>
<td>K-M₃</td>
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</tr>
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<td></td>
<td>K-M₂</td>
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<td>~ 8</td>
</tr>
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</tr>
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<td></td>
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<td>Lₐ₂</td>
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</tr>
<tr>
<td></td>
<td>L₃-N₅,₄</td>
<td>Lₜ₂,₁₅</td>
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</tr>
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<td>~ 5</td>
</tr>
<tr>
<td></td>
<td>M₃-N₁</td>
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</tr>
<tr>
<td>L₂-lines</td>
<td>L₂-M₄</td>
<td>Lₜ₁</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>L₂-N₄</td>
<td>Lₜ₃</td>
<td>~ 20</td>
</tr>
<tr>
<td></td>
<td>L₂-M₁</td>
<td>Lₜ₁</td>
<td>~ 3</td>
</tr>
<tr>
<td></td>
<td>L₂-O₁</td>
<td>Lₜ₃</td>
<td>~ 3</td>
</tr>
<tr>
<td>L₁-lines</td>
<td>L₁-M₃</td>
<td>Lₜ₃</td>
<td>100</td>
</tr>
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</tr>
<tr>
<td></td>
<td>L₁-N₃</td>
<td>Lₜ₃</td>
<td>~ 30</td>
</tr>
<tr>
<td></td>
<td>L₁-N₂</td>
<td>Lₜ₂</td>
<td>~ 30</td>
</tr>
<tr>
<td>M-lines</td>
<td>M₅-N₇</td>
<td>Mₛ₁</td>
<td></td>
</tr>
<tr>
<td></td>
<td>M₅-N₆</td>
<td>Mₜ₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>M₅-N₆</td>
<td>Mₜ₂</td>
<td></td>
</tr>
</tbody>
</table>

![Graph showing variation of characteristic line wavelengths with atomic number.](image)

Fig. 3.7. Variation of characteristic line wavelengths with atomic number.
Each electron in an atom can be defined by four quantum numbers. The first of these quantum numbers is the principal quantum number $n$, which can take all integral values. When $n$ is equal to 1, the level is referred to as the K level; when $n$ is 2, the L level, and so on. $\ell$ is the angular quantum number and this can take all values from $(n - 1)$ to zero. $m$ is the magnetic quantum number and can take values from $+\ell$ to $-\ell$. $s$ is the spin quantum number with a value of $\pm \frac{1}{2}$. The total momentum $J$ of an electron is given by the vector sum of $\ell + s$. Since no two electrons within a given atom can have the same set of quantum numbers, a series of levels or shells can be constructed. Table 3.2 lists the atomic structures of the first three principal shells. The first shell, the K-shell, has a maximum of two electrons and these are both in the 1s level (orbital). Since the value of $J$ must be positive in this instance the only allowed value is $+\frac{1}{2}$. In the second shell, the L shell, there are eight electrons: two in the 2s level and six in the 2p levels. In this instance $J$ has a value of $\frac{1}{2}$ for the 1s level and $\frac{3}{2}$ or $\frac{1}{2}$ for the 2p level, thus giving a total of three possible L transition levels. These levels are referred to as L$_1$, L$_2$ and L$_3$ respectively. In the M level, there are a maximum of 18 electrons: 2 in the 3s level, 8 in the 3p level and 10 in the 3d level. Again, with the values of $\frac{3}{2}$ or $\frac{1}{2}$ for $J$ in the 3p level and $\frac{5}{2}$ and $\frac{3}{2}$ in the 3d level, a total of five M transition levels are possible (M$_1$ to M$_5$). Similar rules can be used to build up additional levels: N, O, etc.

The selection rules for the production of normal (diagram) lines require that the principal quantum number must change by at least one ($\Delta n \geq 1$), the angular quantum number must change by only one ($\Delta \ell = \pm 1$), and the $J$ quantum number must change by zero or one ($\Delta J = 0, \pm 1$). Application of the selection rules indicates that in, for example, the K series, only L$_2$ → K and L$_3$ → K transitions are allowed for a change in the principal quantum number of one. There are equivalent pairs of transitions for $n = 2$, $n = 3$, $n = 4$, etc. Figure 8 shows the lines that are observed in the K series. Three groups of lines are indicated. The normal lines are shown on the left-hand side, consisting of three pairs of lines from the L$_2$/L$_3$, M$_1$/M$_3$ and N$_2$/N$_3$ sub-shells respectively.
While most of the observed fluorescent lines are normal, certain lines may also occur in X-ray spectra that, at first sight, do not abide to the basic selection rules. These lines are called forbidden lines; they arise from outer orbital levels where there is no sharp energy distinction between orbitals. As
an example, in the transition elements, where the 3d level is only partially filled and is energetically similar to the 3p levels, a weak forbidden transition (the $\beta_5$) is observed. A third type are satellite lines arising from dual ionizations. Following the ejection of the initial electron in the photoelectric process, a short, but finite, period of time elapses before the vacancy is filled. This time period is called the lifetime of the excited state. For the lower atomic number elements, this lifetime increases to such an extent that there is a significant probability that a second electron can be ejected from the atom before the first vacancy is filled. The loss of the second electron modifies the energies of the electrons in the surrounding sub-shells, and thus X-ray emission lines with other energies are produced. For example, instead of the K$\alpha_1$/K$\alpha_2$ line pair, a double ionized atom will give rise to the emission of satellite lines such as the K$\alpha_3$/K$\alpha_4$ and the K$\alpha_5$/K$\alpha_6$ pairs. Since they are relatively weak, neither forbidden transitions nor satellite lines have great analytical significance; however, they may cause some confusion in the qualitative interpretation of spectra and may sometimes be misinterpreted as being analytical lines of trace elements.

3.2.7 Figures-of-merit for XRF spectrometers

a. Analytical Sensitivity

When XRF analysis of thin film samples is performed (i.e., in samples where the product $\rho d$ of sample thickness $d$ and sample density $\rho$ is so small that absorption of the incoming exciting and of the outgoing fluorescent radiation in the material can be neglected – see Section C.), there is a linear relation between the collected net X-ray intensity $N_i$ of a given characteristic line of element $i$ and the irradiated mass $m_i$, which usually is also proportional to the concentration $c_i$ of that element in the sample:

$$N_i = S_i \cdot m_i \cdot t = S_i \cdot c_i \cdot t$$ (8)
The proportionality constants $S_i$ for the various elements are called the sensitivity coefficients of the XRF spectrometer for determination of these elements (expressed in counts/s/(g/cm$^3$)) and are important figures-of-merit of the instrument. In Fig. 3.9, the variation with atomic number of the sensitivity of a WDXRF spectrometer is plotted, for the case where either the $K_\alpha$ ($10 < Z_i < 60$) or $L_\alpha$ ($40 < Z_i < 80$) peak intensities are used as analytical signals. By a selection of the excitation conditions (tube anode material, excitation voltage), the shape and location of the maximum in the sensitivity curve can be influenced to suit the needs of the application at hand.

Instead of using the X-ray intensity collected during a specific time $t$, it is often more convenient to use the net X-ray count rate $R_i$:

$$
R_i = N_i / t = S_i \cdot c_i
$$

### b. Detection and determination limits

In reality, it is not possible to directly measure the net peak intensity $N_i$; rather, a total intensity $T_i = N_i + B_i$ is measured (see also Fig. 3.27). The background intensity $B_i$ can be written as the sum of various contributions:

$$
B_i = B_i^{\text{scatter}} + B_i^{\text{detector}} + \sum_{j \neq i} B_{ij}^{\text{overlap}} + B_i^{\text{blank}}
$$

Fig. 3.9. Variation of sensitivity coefficients with atomic number for a WDXRF spectrometer.
where $B_{i,\text{scatter}}$ denotes the contribution to the spectral background below the analytical line of element $i$ due to scattering of the primary radiation in the sample itself, in the sample environment gas (air or Helium, if any) and (in some cases) on the sample holder materials. These phenomena cause a continuous background upon which the characteristic peaks are superimposed. $B_{i,\text{detector}}$ denotes the background contribution in the same energy/wavelength region due to detector artifacts, $B_{i,j,\text{overlap}}$ is the contribution to the peak intensity resulting from unresolved overlap between lines of an element $j \neq i$ and the analytical line of element $i$ and $B_{i,\text{blank}}$ denotes the contributions to the peak intensity of element $i$ not originating from the sample, i.e. a blank value.

When the magnitude of $B_i$ is experimentally determined and this measurement is repeated $n$ times, the results will be distributed around a mean value $<B_i>$ with a standard deviation $s_B$. In modern instruments, most sources of systematic and random errors (e.g. due to mechanical or electrical instabilities) are small compared to the inherent uncertainty on the intensity measurements resulting from counting statistics. When $B_i$ is obtained by means of a counting procedure (which usually is the case), Poisson (or counting) statistics govern the measurements so that $s_B^2 = <B_i>$.

The Union of Pure and Applied Chemistry (IUPAC) defines the limit of detection as “the lowest concentration level than can be determined to be statistically significant from an analytical blanc”. The lowest net X-ray intensity $N_{i,\text{LD}}$ that still can be distinguished in a statistically significant manner from the average background level can be written as:

$$N_{i,\text{LD}} = <B_i> + k s_B$$

where $k$ is an integer constant depending on the significance level considered.
The limit of detection concentration \( c_{i,LD} \) corresponding to \( N_{i,LD} \) can be written as:

\[
c_{i,LD} = \frac{N_{i,LD} - \langle B_i \rangle}{S_i \cdot t} = \frac{k S_B}{S_i \cdot t} = \frac{k R_B}{S_i \cdot \sqrt{t}} \tag{12}
\]

where \( R_B = \langle B_i \rangle / t \) is the background count rate. When the irradiation of a standard sample (with known concentration \( c_i \)) during a time \( t \) results in net and background intensities \( N_{i,\text{std}} \) and \( B_{i,\text{std}} \), so that the sensitivity \( S_i \) can be approximated by the ratio \( N_{i,\text{std}} / c_{i,\text{std}} / t \), it follows that the lowest detectable concentration (or relative detection limit) \( c_{i,LD} \) can be estimated from this measurement by using the relation:

\[
c_{i,LD} \approx c_{i,\text{std}} \frac{k \sqrt{B_{i,\text{std}}}}{N_{i,\text{std}}} \tag{13}
\]

When during such an experiment, a known mass \( m_{i,\text{std}} \) was irradiated, the lowest detectable mass (or absolute detection limit) \( m_{i,LD} \) is can be calculated by means of:

\[
m_{i,LD} \approx m_{i,\text{std}} \frac{k \sqrt{B_{i,\text{std}}}}{N_{i,\text{std}}} \tag{14}
\]

Relative detection limits are useful figures-of-merit for bulk XRF equipment, where it usually is relevant to know the lowest concentration level at which the spectrometer can be used for qualitative or quantitative determinations. In instruments where very small sample masses are being irradiated (e.g., in the pg range for microscopic XRF (µ-XRF) and total-reflection XRF (TXRF)), the absolute detection limit is another useful figure-of-merit since that provides information on the minimal sample mass than can be analysed in a given setup.
In the literature, usually detection limit values for \( k = 3 \) (corresponding to a statistical confidence level of 99\%) are reported. A related figure-of-merit is the determination limit which is defined as the lowest concentration (or mass) at which a quantitative determination with a relative uncertainty of at least 10\% is possible. This quantity can be calculated by setting \( k = 10 \) in the above expressions.

In Table 3.3, as an example, relative LD values for trace element obtained by means of WDXRF in different matrices are listed. In Fig. 3.10, a plot of typical absolute LD values for TXRF spectrometers is shown.
Table 3.3. WDXRF obtained relative detection limits (in µg/g) in various matrix and using different instruments.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Element</th>
<th>c_{LD}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terephthalic acid</td>
<td>Fe</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>0.18</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Mg</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>1.3</td>
</tr>
<tr>
<td>Al-Mg alloy</td>
<td>Mg</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Si</td>
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</tr>
<tr>
<td></td>
<td>Ti</td>
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</tr>
<tr>
<td></td>
<td>Mn</td>
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<tr>
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<td>Cu</td>
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<tr>
<td>Cement</td>
<td>Na₂O</td>
<td>36</td>
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<tr>
<td></td>
<td>MgO</td>
<td>27</td>
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<td></td>
<td>Al₂O₃</td>
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</tr>
<tr>
<td></td>
<td>SiO₂</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>SO₃</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>P₂O₅</td>
<td>32</td>
</tr>
<tr>
<td>Low-Alloy Steel</td>
<td>C</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Al</td>
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</tr>
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<td></td>
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<td></td>
<td>Cr</td>
<td>2</td>
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<tr>
<td>Copper Alloys</td>
<td>Be</td>
<td>0.20%</td>
</tr>
</tbody>
</table>
3.3 Instrumentation

While most of the early work in X-ray spectrometry was carried out using electron excitation, today, use of electron-excited X-radiation is restricted mainly to X-ray spectrometric attachments to electron microscopes. Most modern stand-alone X-ray spectrometers use X-ray excitation sources rather than electron excitation. All conventional X-ray spectrometers comprise three parts: the primary source unit, the spectrometer itself and the measuring electronics.

X-ray fluorescence spectrometry typically uses a polychromatic beam of short wavelength/high energy photons to induce the emission of longer wavelength/ lower energy characteristic lines in the sample to be analyzed. Modern X-ray spectrometers may use either the diffracting power of a single crystal to isolate narrow wavelength bands (wavelength dispersive XRF - WDXRF) or an energy-selective detector may be employed to isolate narrow energy bands (energy dispersive XRF – EDXRF) from the polychromatic radiation (including characteristic radiation) that is produced in the sample.

Because the relationship between emission wavelength and atomic number is known, isolation of individual characteristic lines allows the unique identification of an element to be made and elemental concentrations can be estimated from characteristic line intensities. Thus this technique is a means of material characterization in terms of chemical composition.

Wavelength dispersive XRF instrumentation is almost exclusively used for (highly reliable and routine) bulk-analysis of materials, e.g., in industrial quality control laboratories. In the field of energy-dispersive XRF instrumentation, next to the equipment suitable for bulk analysis, several important variants have evolved in the last 20 years. Both total reflection XRF (TXRF) and micro-XRF are based on the spatial confinement of the primary X-
ray beam so that only a limited part of the sample (+ support) is irradiated. This is realized in practice by the use of dedicated X-ray sources, X-ray optics, and irradiation geometries.

3.3.1 X-ray sources

Four different types of X-ray sources are being employed in X-ray analysis: (a) sealed X-ray tubes and (b) radioactive sources are the most commonly employed, while to a lesser extent primary X-rays produced in (c) rotating anode tubes and (d) synchrotron radiation facilities is also utilized for analytical purposes.

Most commercially available X-ray spectrometers utilize a sealed X-ray tube as an excitation source, and these tubes typically employ a heated tungsten filament to induce the emission of thermionic electrons in a vacuum chamber. After acceleration by means of a high voltage $V$, the electrons are directed towards a layer of high purity metal (e.g., Cr, Rh, W, Mo, Rh, Pd, ...) that serves as anode. In the metal layer, a bremsstrahlung continuum is produced, onto which the characteristic lines of the anode material are superimposed. The broad band radiation is well suited for the excitation of the characteristic lines of a wide range of atomic numbers. The higher the atomic number of the anode material, the more intense the beam of radiation produced in the tube. Fig. 3.11 shows a schematic cross-section of a sealed X-ray tube.

In typical X-ray tubes employed in XRF spectrometers, accelerating voltages of 25-50 kV are used, while electron currents in the range 20-50 mA are employed. For WDXRF, frequently, 3 kW X-ray tubes are used; in EDXRF spectrometers, depending on the manner of sample excitation, tubes in the 50-1000 W range are employed. The efficiency of an X-ray tube is relatively low: only about 1% of the electric power is converted into X-rays, the rest is dissipated as heat.
Accordingly, the tube anode of high power tubes (> 100 W) usually is water-cooled to about melt-down of the metal block. A key factor in the design of a X-ray tube is the maximum powder loading (expressed in W/mm²) it can stand. The high-voltage power supplies used together with X-ray tubes are highly stable so that a wide conical X-ray beam of nearly constant intensity (to within a few % relative) is being emitted. For applications requiring higher power levels as 3 kW, rotating rather than fixed anode tubes are employed. In these devices, the anode is a fast-spinning water-cooled metal cylinder covered with the desired anode material. During each revolution of the anode, only a small area on the surface is bombarded by the electrons during a short fraction of the time, so that the rest of the period can be used for heat removal. Rotating anode tubes that can be operated up to a total power of 18 kW are commercially available.

The emission spectrum of a X-ray tube (see Fig. 3.6) consists of two components: a *bremssstrahlung* continuum upon which the characteristic lines of the anode material (that becomes ionized as a result of the electron
bombardment) are superimposed. The shape of the emission spectrum can be modified by changing the electron acceleration voltage.

Radioactive \(\alpha\)-, \(\beta\)-, and \(\gamma\)-sources may also be employed for (ED)XRF analysis. Generally, these sources are very compact compared to X-ray tubes and can, e.g., be used in portable analysis systems. \(\alpha\)-sources are suited for the analysis of low atomic number elements. Frequently used sources are \(^{244}\text{Cm}\), with a half-life \((t_{1/2})\) of 17.8 y that emits 5.76 and 5.81 MeV \(\alpha\)-particles, and \(^{210}\text{Po}\), having a half-life of 138 days and emitting 5.3 MeV \(\alpha\)’s.

\(\beta\)-sources can also be employed, either for direct EDXRF excitation of a sample or for producing \(\text{bremssstrahlung}\) radiation in a target to be used for subsequent sample excitation. \(^{22}\text{Na}\) \((t_{1/2} = 2.6 \text{ y})\), \(^{85}\text{Kr}\) \((t_{1/2} = 10.7 \text{ y})\) and \(^{63}\text{Ni}\) \((t_{1/2} = 100 \text{ y})\) are \(\beta\)-emitters that can be used for the former purpose, emitting resp. \(\beta\)-particles of ca. 550, 670 and 66 keV. For \(\text{bremssstrahlung}\) production, \(^{147}\text{Pm}\) \((t_{1/2} = 2.6 \text{ y}, 225 \text{ keV})\) in combination with a Zr target and \(^{3}\text{H}\) \((t_{1/2} = 12.4 \text{ y}, 19 \text{ keV}, \text{Ti target})\) are useful.

In Table 3.4, some characteristics of radio sources emitting X-ray or \(\gamma\)-ray lines are listed. The X-ray emitting sources usually contain nuclides that decay by means of the electron-capture mechanism. During the decay, a inner shell electron is captured by the neutron-deficient nucleus, transforming a proton in a neutron. This results in a daughter nuclide that has a vacancy in one of its inner shells, which results in the emission of corresponding characteristic radiation. For example, when a \(^{55}\text{Fe}\)-nucleus (26 protons and 29 neutrons) captures a K-electron and becomes a \(^{55}\text{Mn}\) nucleus, a Mn K-L\(_{3,2}\) (Mn-K\(_{\alpha}\)) or K-M\(_{3,2}\) (Mn-K\(_{\beta}\)) photon will be emitted. Other sources (such as \(^{241}\text{Am}\) or \(^{57}\text{Co}\)) emit \(\gamma\)-rays of suitable energy as a result of different nuclear transformations.
Table 3.4. Radioactive sources used for XRF analysis (flux in photons/s/sr).

<table>
<thead>
<tr>
<th>Radio isotope</th>
<th>Half-life (years)</th>
<th>X-ray or γ-ray energy (keV)</th>
<th>Flux (photons/s/sr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{55}$Fe</td>
<td>2.7</td>
<td>5.9-6.5 (Mn-K X-rays)</td>
<td>$7 \times 10^6$</td>
</tr>
<tr>
<td>$^{244}$Cm</td>
<td>88</td>
<td>14.6-22 (U L X-rays)</td>
<td></td>
</tr>
<tr>
<td>$^{109}$Cd</td>
<td>1.3</td>
<td>22-25 (Ag K X-rays)</td>
<td>$8 \times 10^6$</td>
</tr>
<tr>
<td>$^{125}$I</td>
<td>0.16</td>
<td>27-32 (Te K X-rays)</td>
<td></td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>433</td>
<td>59.6 (γ-ray)</td>
<td>$6 \times 10^7$</td>
</tr>
<tr>
<td>$^{153}$Gd</td>
<td>0.66</td>
<td>41.48 (Eu-K X-rays)</td>
<td>$4 \times 10^8$</td>
</tr>
<tr>
<td>$^{57}$Co</td>
<td>0.74</td>
<td>122.136 (γ-ray)</td>
<td>$4 \times 10^6$</td>
</tr>
</tbody>
</table>

In Fig. 3.12, the range of elements that can be usefully analyzed by means of various radioactive and X-ray tubes sources is summarized.

Fig. 3.12. Range of elements that can be analyzed using (a) radioactive sources, (b) X-ray tubes with different anodes, showing excitation of K- and L-lines.
In a number of specialized cases, XRF experiments also make use of synchrotron sources. Synchrotron radiation (SR) is produced by high-energy (GeV) relativistic electrons or positrons circulating in a storage ring. This is a very large, quasi-circular vacuum chamber where strong magnets force the particles on closed trajectories. X-radiation is produced during the continuous acceleration (change in velocity vector in this case) of the particles. SR-sources are several (6-12) orders of magnitude more bright than X-ray tubes, have a natural collimation in the vertical plane and are linearly polarized in the plane of the orbit. The spectral distribution is continuous, and the most simple way of employing SR is to use the full white beam to irradiate the sample (see below – micro-XRF). By proper monochromatization, it is possible to employ selective excitation of a series of elements in the sample, yielding optimal detection conditions (see below – TXRF). An additional advantage is the high degree of polarization of SR, causing spectral backgrounds due to scatter to be greatly reduced when the detector is placed at 90° to the primary beam and in the storage ring plane. The combination of a high primary beam intensity and low spectral background causes DL values of SRXRF to go down to the ppb level (see, e.g., Fig. 3.24). A disadvantage of the use of SR is that the source intensity decreases with time (due to a gradual loss of orbiting particles in between ring refills) so that measurement of unknown samples must be bracketed between standards and/or by continuously monitoring the primary beam intensity.

3.3.2 X-ray detectors

As any radiation detector, an X-ray detector is a transducer for converting X-ray photon energy into easily measurable and countable voltage pulses. All detector types work through a process of photoionization in which interaction between the entering X-ray photon and the active detector material produces a number of electrons. By means of a capacitor and a resistor, the current produced by the electrons in converted to a voltage pulse, in such a way that
one digital voltage pulse is produced for each X-ray photon that enters the
detector.

Next to being sensitive to photons of the appropriate energy range, there are
two other important properties that the ideal detector should possess:
proportionality and linearity. A detector is said to be proportional when the
height of the voltage pulse that is produced upon entry of a photon, is
proportional to the energy of the photon. Proportionality is needed when,
through pulse-height selection, only pulses of a particular height, i.e.
corresponding to X-ray photons within a specific energy band, are to be
measured.

When the rate with which voltage pulses are being recorded is the same as the
rate with which X-ray photons enter the detector, the latter is said to have a
linear response. This property is important when the recorded count rates of
various X-ray lines are to be used as measures of the photon intensities of
these lines produced in a sample.

The detector resolution is the precision/repeatability with which the energy
of a specific type of X-ray photons (e.g., the Mn-K\textsubscript{\alpha} line at 5.9 keV) can be
determined and is therefore a measure of the capability of the detector to
distinguish between X-rays of very similar energy but different origin (e.g.,
the As- K\textsubscript{\alpha 1} line at 10.543 keV and the Pb-L\textsubscript{\alpha 1} line at 10.549 keV).

In wavelength dispersive spectrometers, gas flow proportional counters (for
long wavelengths, \(\lambda > 0.2 \text{ nm}\)) and scintillation counters (for wavelengths
shorter than 0.2 nm) are used to count X-rays. Both types of detectors usually
are combined in a tandem detector that covers the entire wavelength range
used in WDXRF spectrometry. Since neither of these detectors has sufficient
resolution to separate multiple wavelengths/energies on its own, they are
employed together with an analyzing crystal. In case of energy-dispersive
spectrometry, solid-state detectors of higher resolution are used.
A gas flow proportional counter (see Fig. 3.13a) consists of a cylindrical tube about 2 cm in diameter, carrying a thin (25–50 mm) wire along its radial axis. The tube is filled with a mixture of inert gas and quench gas – typically 90% argon/10% methane (P-10). The cylindrical tube is grounded and a voltage of ca 1400–1800 V is applied to the central wire. The wire is connected to a resistor shunted by a capacitor. An X-ray photon entering the detector produces a number of ion pairs ($n$), each comprising one electron and one Ar$^+$ ion. The first ionization potential for argon is about 16 eV, but competing processes during the conversion of photon energy to ionization cause the
average energy required to produce an ion pair to be greater than this amount. The fraction relating the average energy to produce one ion pair, to the first ionization potential, is called the Fano factor $F$. For argon, $F$ is between 0.5 and 0.3 and the average energy $\epsilon$ required to produce one primary ion pair is equal to 26.4 eV. The number of ion pairs produced by a photon of energy $E$ will equal:

$$n = E/\epsilon$$

(15)

Following ionization, the charges separate with the electrons moving towards the (anode) wire and the argon ions to the grounded cylinder. As the electrons approach the high field region close to the anode wire they are accelerated sufficiently to produce further ionization of argon atoms. Thus a much larger number $N$ of electrons will actually reach the anode wire. This effect is called gas gain, or gas multiplication, and its magnitude is given by $M = N/n$. For gas flow proportional counters used in X-ray spectrometry $M$ typically has a value of around $10^5$. Provided that the gas gain is constant the size of the voltage pulse $V$ produced is directly proportional to the energy $E$ of the incident X-ray photon. In practice not all photons arising from photon energy $E$ will be exactly equal to $V$. There is a random process associated with the production of the voltage pulses and the resolution of a counter is related to the variance in the average number of ion pairs produced per incident X-ray photon.

While the gas flow proportional counter is ideal for measurement of longer wavelengths, it is rather insensitive to wavelengths shorter than about 0.15 nm. For this shorter wavelength region it is common to use a scintillation counter (see Fig. 3.13b). The scintillation counter consists of two parts, the phosphor (scintillator) and the photomultiplier. The phosphor is typically a large single crystal of sodium iodide that has been doped with thallium, denoted as a NaI(Tl) crystal. When X-ray photons fall onto the phosphor,
blue light photons are produced (with a wavelength of 410 nm), where the number of blue light photons is related to the energy of the incident X-ray photon. These visual light photons produce electrons by interaction with the surface of the photocathode in the photomultiplier, and the number of electrons is linearly increased by a series of secondary surfaces, called dynodes, inside the photomultiplier. The current produced by the photomultiplier is then converted to a voltage pulse, as in the case of the gas flow proportional counter. Since the number of electrons is proportional to the energy of the incident X-ray photon, the scintillation counter also has a proportional response. Because of inefficiencies in the X-ray/visual-light/electron conversion processes, the average energy to produce a single event within a scintillation counter is more than a magnitude greater than the equivalent process in a flow counter. For this reason, the resolution of scintillation counters is much worse than that of flow counters.

The output pulses produced by both above-mentioned detectors are further processed by a linear amplifier and a discriminator circuit. Usually the number of pulses is counted during a preset amount of time and the accumulated counts stored in computer memory for display and further processing. The processing of an X-ray event by the detector and its associated electronics takes a finite amount of time. After the arrival of one X-ray the detection system is said to be ‘dead’ during this length of time, because X-rays arriving within this dead period will not be counted. The dead time is of the order of 200 to 300 ns after the arrival of each photon; this implies that count rates up to $10^6$ photons per second can be handled.

The detectors used in the various forms of EDXRF are semiconductor detectors. Conventionally, two types, i.e. lithium drifted silicon (Si(Li)) and hyperpure germanium (HP-Ge) detectors are used. Their main advantages are their compact size, the non-moving system components, and relatively good energy resolution, which optimally is of the order of 120 eV at 5.9 keV.
Because of their operation principles, these detectors have an inherent simultaneous multielement capacity, which leads to a short measuring time for all elements as the detectors select the energy and collect counts at the same time. Disadvantages include the need for liquid nitrogen (LN\textsubscript{2}) cooling during operation, the necessity of having a relatively thin (8–25 \(\mu\)m) Be window and the fact that the maximum processable number of counts is limited to about 40,000 cps. This figure can be increased to 100,000 cps, but with loss of optimal performance characteristics.

The detector crystal itself is a disk of very pure Si or Ge with dimensions of 4–10-mm diameter and 3–5-mm thickness. Even careful production of the Si ingots the disk are cut from will still leave some trace impurities in the Si lattice. To compensate and bind all free electrons, lithium ions are drifted (allowed to diffuse at elevated temperature) into the silicon crystal to neutralize the Si crystal defects in a particular zone, the so-called intrinsic zone. Afterwards, Au contacts are evaporated onto the crystal and a reverse voltage applied. In the crystal, the energy difference \(\varepsilon\) (band gap) between the valence and conduction band is 3.8 eV. At room temperature, the conduction band is partially populated so that the crystal is a (semi)conductor. To keep the leakage current as low as possible, the crystal is cooled with LN\textsubscript{2} by placing it a vacuum cryostat. At \(-196^\circ\text{C}\) almost all electrons remain in the valence band. The radiation to be measured needs to enter the cryostat through a thin entrance window, usually made of Be. By applying a reverse voltage to the charge carrier free intrinsic zone, an absorbed X-ray photon is converted into charge by ionization. Electrons are promoted from the valence to the conduction band, leaving “positive holes” in the valence band; thus the crystal temporarily becomes conducting. \(n = E/\varepsilon\) of electron-hole pairs are created. The electrons and holes are quickly swept to the contact layers by the electric field created by the applied reverse bias on the crystal.
Fig. 3.14 shows the operation principle schematically. The charge induces a signal at the gate of a cooled field effect transistor (FET) that is the input stage of a charge sensitive preamplifier. The output signal is fed to a pulse processor that shapes the pulse and amplifies it further. This signal is in the range up to 10 V and is proportional to the energy of the absorbed photon. The pulse height is digitized by means of an analog-to-digital converter (ADC) and the resulting digital value stored in a multichannel analyzer (MCA). This is an array of memory cells, called channels; by using the digital value associated with a single event as address offset into the memory array, the content of the appropriate channel is incremented with one count. Thus, all detector events having the same pulse height are stored in the same channel. For example, upon entry in the detector of a Cu-Kα photon \( (E = 8.05 \text{ keV}) \), 2117 electron-hole pairs will be generated, which may lead to the formation of a preamplifier voltage pulse of, e.g., 42.0 mV. After further amplification and shaping, this is converted into a bell-shaped pulse of 4.20 V; the pulse-height is then digitized by an ADC, resulting for instance in a digital number of 420. Ultimately, this causes the content of channel 420 to be incremented with one count. After readout, the MCA memory (typically 1024 or 2048 channels in size, each corresponding to a 10-20 eV wide energy range) yields a pulse-height distribution of the detected events or an energy-dispersive X-ray spectrum, as shown in Fig. 3.15.
In the spectra, always a broadening of the X-ray lines can be observed, i.e. the counts associated with photons of a specific energy, which normally should end up in a single channel, are distributed in a quasi-gaussian fashion over several adjacent channels in the spectrum, thus giving rise to a bell-shaped X-ray peak in the spectrum. This line-broadening is caused by statistical fluctuations in the number of electron-hole pairs created when a X-ray photon of a given energy enters the detector; electronic noise in the amplifiers cause the uncertainty on the pulse-height to increase further. Even under conditions in which all noise contributions in the electronics are minimized, the line broadening remains a significant phenomenon, causing frequent peak overlap to occur in X-ray spectra, e.g., between lines of adjacent elements such as the Mn-K\(_\beta\) and Fe-K\(_\alpha\) peaks. The resolution of energy-dispersive detectors conventionally is expressed as the full-width-at-half-maximum of the Mn-K\(_\alpha\) (Mn K-L\(_{2,3}\)) peak (at 5.98 keV) and typically is around 150 eV. In the most optimal case, this value can be also low as 120 eV. The time to process and X-ray event (dead time) is of the order of 10 to 30 µs; conventional EDXRF spectrometers can therefore only operate at count rates up to 40000 counts per second. In view of the presence of a Be window in the detector cryostat, X-ray photons below 2 keV are hard to detect in a conventional Si(Li) detector, although thin-window models are commercially available.

![Energy-dispersive XRF spectrum obtained from a multi-element standard in TXRF mode.](image)
Roughly since 1995, several types of compact and thermoelectrically cooled ED detectors have become available. The most significant advantage of these detectors is that they do not require liquid nitrogen cooling, allowing the instrument they are incorporated into to be much smaller. These type of detectors is suitable for employment in portable equipment.

Thermoelectrically cooled Si-PIN, Cd$_{1-x}$Zn$_x$Te (CZT) and HgI$_2$ detectors are fairly inexpensive devices. The currently available Si-PIN diode detectors mostly have a thickness of about 300 $\mu$m which makes the detector useful up to X-ray energies of 20 keV and an energy resolution in the range 180-200 eV at Mn-K$_{\alpha}$, i.e., slightly worse than that of Si(Li) or HPGe detectors. Versions with 500 $\mu$m thickness or larger active areas (up to 25 mm$^2$ vs. the standard 5-10 mm$^2$) are now (2001) becoming available, but still have resolutions in the 200-250 eV range at Mn-K$_{\alpha}$. CZT detectors are targeted towards the higher energy range with a thickness of up to 2 mm, allowing efficient detection of X-rays up to 150 keV with a resolution of ca 250 eV at Mn-K$_{\alpha}$ (5.9 keV) and 1 keV at 60 keV. Similarly, HgI$_2$ detectors (with thicknesses of a few millimeters) can also be used in this range with a resolution of ca 200 eV at Mn-K$_{\alpha}$.

A very promising type of solid-state detector is the solid-state drift chamber (SSD) detector, featuring excellent energy resolution at high count rates. A FWHM below 140 eV at 5.9 keV can be achieved with thermoelectrical cooling (Peltier effect). SSDs exist in a large variety of sizes up to 2 cm$^2$ diameter. They still show excellent spectroscopical behaviour at count rates as high as $2.10^6$ counts/cm$^2$/s. The compact design, the relatively low price, the absence of the need for liquid nitrogen for cooling, the high count rate capability and the non-sensitivity to noise pick-up make these systems attractive alternatives to conventional semiconductor detectors.

The resolution of a number of different of X-ray detectors in the range 1-100 keV (ca 1 - 0.01 nm) are compared in Fig. 3.16. It is clear that scintillators and
proportional counters are not even able to separate the $K_{\alpha}$-lines of adjacent elements whereas this is the case for most of the solid-state detectors.

![Energy-resolution graph](image)

**Fig 3.16.** Energy-resolution (expressed as FWHM of the $K_{\alpha}$ line of a given energy), of different X-ray detectors in the 1-100 keV range. The difference in $K_{\alpha}$ line energy between adjacent elements is also shown (symbols).

### 3.3.3 Wavelength dispersive XRF

A typical WDXRF system consists of an X-ray tube, a specimen support holder, a primary collimator, an analyzing crystal and a tandem detector. The typical WDXRF irradiation/detection geometry is shown in Fig. 3.17. Wavelength-dispersive spectrometers employ diffraction by a single crystal to separate characteristic wavelengths emitted by the sample. A single crystal of known interplanar spacing $d$ is used to disperse the collimated polychromatic beam of characteristics wavelengths that is coming from the sample, such that each wavelength $\lambda$ will diffract at a specific angle $\theta$, given by Bragg’s law:

$$n\lambda = 2d \sin \theta$$

(16)
where \( n \) is an integer number denoting the order of the diffracted radiation. A goniometer is used to maintain the required \( \theta/2 \) relationship between sample and crystal/detector.

![Schematic drawing of a wavelength-dispersive XRF spectrometer.](image)

Prior to impinging on the analyzer crystal, by means of a collimator or slit, the spread in initial directions of the sample-to-crystal beam is limited. Since the maximum achievable angle on a typical WDXRF spectrometer is around 73°, the maximum wavelength that can be diffracted by a crystal of spacing \( d \) is equal to ca 1.9\( d \).

The angular dispersion \( \frac{d\theta}{d\lambda} \) of a crystal with spacing 2\( d \) is given by:

\[
\frac{d\theta}{d\lambda} = \frac{n}{2d \cos \theta}
\]

(17)

and is therefore inversely proportional to its \( d \)-spacing. This, high dispersion can only be obtained at the expense of reducing the wavelength range covered by a particular crystal. Several crystals therefore are likely to be employed for covering a number of analyte elements. Typically, 4 to 6 different analyzer crystals (with different \( d \)-spacings) and two different
collimators are provided in this type of instrument, allowing for a wide choice in dispersion conditions. The smaller the $d$-spacing of the crystal, the better the separation of the lines, but the smaller the wavelength range that can be covered. The separating power of the crystal spectrometer is dependent upon the divergence allowed by the collimators (which mainly determine the width of the diffracted lines) in the $2\theta$ spectrum, but also the angular dispersion of the analyzing crystal itself and the intrinsic width of the diffraction lines play a role.

In Table 3.5, some characteristics of a few commonly employed analyzer crystals are listed. Classically, large single crystals have been used as dispersive elements. For dispersion of long wavelengths ($> 0.8$ nm), only a limited number of natural materials are available; the most commonly employed is thallium acid phthalate (TAP, $2d = 2.63$ nm), allowing measurement of the Mg, Na, F and O-K lines. As alternative, several other materials with large $2d$-spacings have been used and since the 1980's Layered Synthetic Multilayers (LSMs) are in use. These consist of stacks of alternate electron-rich (e.g. W) and electron-poor (e.g., graphite) layers of atoms or molecules, deposited on a sufficiently smooth substrate. Since the composition and interplanar distance of the LSM to a certain extent can be optimized for particular applications, a factor four to six improvement in peak intensities compared to TAP crystals can be achieved.

Table 3.5. Analyzing crystals used in wavelength-dispersive X-ray spectrometry

<table>
<thead>
<tr>
<th>Crystal</th>
<th>planes</th>
<th>2d (nm)</th>
<th>K-line range</th>
<th>L-line range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Fluoride (LiF)</td>
<td>220</td>
<td>0.2848</td>
<td>&gt; Ti</td>
<td>&gt; La</td>
</tr>
<tr>
<td>Lithium Fluoride (LiF)</td>
<td>200</td>
<td>0.4028</td>
<td>&gt; K</td>
<td>&gt; Cd</td>
</tr>
<tr>
<td>Pentaerythritol (PET)</td>
<td>002</td>
<td>0.8742</td>
<td>Al - K</td>
<td>-</td>
</tr>
<tr>
<td>Thallium acid phthalate (TAP)</td>
<td>001</td>
<td>2.64</td>
<td>F - Na</td>
<td>-</td>
</tr>
<tr>
<td>LSMs</td>
<td>-</td>
<td>5 – 12</td>
<td>Be - F</td>
<td>-</td>
</tr>
</tbody>
</table>
Among wavelength dispersive spectrometers, a distinction can be made between single-channel instruments and multichannel spectrometers. In the former type of instrument, a single dispersive crystal/detector combination are used to sequentially measure the X-ray intensity emitted by a sample at a series of wavelengths when this sample is irradiated with the beam from a high power (2-4 kW) X-ray tube. In a multi-channel spectrometer, many crystal/detector sets are used to measure many X-ray lines/elements simultaneously.

Single channel instruments are also referred to as scanning spectrometers; this type is the most common. During an angular scan, the angle $\theta$ between sample and analyzer crystal is continuously varied; in order to maintain an identical angle between analyzer crystal and detector, the latter moves at the double angular speed as the crystal. In this manner, X-ray intensity vs. 2$\theta$ diagrams are obtained. By means of tables, the recorded peaks can be assigned to the characteristic lines of one or more elements. In Fig. 3.18, a typical 2$\theta$-spectrum obtained from a brass sample is shown.

Fig. 3.18. Wavelength dispersive X-ray spectrum of a brass sample, showing the characteristic lines of the major elements Cu and Zn, and of the minor constituents Cr, Fe, Ni and Pb, superimposed on a continuous background.

Simultaneous wavelength-dispersive spectrometers were introduced in the early 1950s, and sequential systems about a decade later. At this time, about 30,000 or so wavelength-dispersive instruments have been supplied
commercially. The two major categories of wavelength-dispersive X-ray spectrometers differ mainly in the type of source used for excitation, the number of elements that they are able to measure at one time, the speed at which they collect data and their price range. For high specimen throughput quantitative analysis where speed is of the essence, and where high initial cost can be justified, simultaneous wavelength-dispersive spectrometers are optimal. For more flexibility, where speed is important but not critical and where moderately high initial cost can be justified, sequential wavelength-dispersive spectrometers are probably more suited. Both of the instruments are, in principle at least, capable of measuring all elements in the periodic classification from $Z = 9$ (F) and upwards, and most modern wavelength-dispersive spectrometers can do some useful measurements down to $Z = 6$ (C). Both can be fitted with multisample handling facilities and automated. Both are capable of precision of the order of a few tenths of 1% and both have sensitivities down to the ppm level. Single-channel wavelength-dispersive spectrometers are typically employed for both routine and nonroutine analysis of a wide range of products, including ferrous and nonferrous alloys, oils, slags and sinters, ores and minerals and thin films. These systems are very flexible but, relative to multichannel spectrometers, are somewhat slow. The multichannel wavelength-dispersive instruments are used almost exclusively for routine, high throughput analyses where there is need of fast accurate analysis, but where flexibility is of no importance.

3.3.4 Energy dispersive XRF

Energy-dispersive spectrometers became commercially available in the early 1970s with the advent of high resolution solid state detectors; today there are of the order of 20,000 units in use. In principle, EDXRF instruments have a much simpler mechanical design than WDXRF instruments, as the detection system does not include any moving parts and the solid-state detector (most commonly a Si(Li) detector) itself acts as a dispersion agent. The high
geometrical efficiency of the semiconductor detector permits a great variety in excitation conditions. The manner in which the radiation that originally exits from the X-ray tube is ‘pretreated’ before it reaches the sample varies according to the type of EDXRF instrument. The final analytical capabilities and in particular the LD values that can be attained by the instrument strongly depend on the sophistication with which this is done.

In Fig. 3.19a, the most simple of ED-XRF instrumental configurations is shown. A low power X-ray tube (e.g., 50 W) and a Si(Li) detector are both placed at an angle of 45° with respect to the sample. Collimators are used to confine the excited and detected beam to a sample area between 0.5 and 2 cm². In such a ‘direct-excitation’ configuration, the distance between the components can be fairly small (typically a few cm) and since both the tube anode lines and the bremsstrahlung-component of tube output spectrum are used to irradiate the sample, only a limited tube power is required. Since the bremsstrahlung continuum not only ensures a uniform excitation of many elements, but also causes a significant scatter background to be present in the recorded EDXRF spectra, most direct-excitation systems are equipped with a set of primary beam filters to alter the tube spectrum. By selection of an appropriate filter, the excitation conditions for a particular range of elements can be optimized. In order to facilitate the determination of low-Z element,
commercial systems can be either evacuated or flushed with He, thus reducing the absorption of low energy radiation and scatter.

The schematic of a ‘secondary target’ EDXRF system is shown in Fig. 3.19b. In such a configuration, a high power (1 kW) X-ray tube irradiates a metal disk (the secondary target, e.g., made of Mo), causing it to emit its own characteristic radiation lines (Mo-K\(_{\alpha}\) and Mo-K\(_{\beta}\)). This ‘bichromatic’ fluorescent radiation is then used to excite the sample to be examined. The advantage of the secondary target scheme is that, as a result of the bichromatic excitation, the background in the resulting EDXRF spectra is significantly lower as in the direct excitation case. This leads to better detection limits. By using a filter that preferentially absorbs the K\(_{\beta}\) component of the secondary target radiation (e.g., a Zr foil in case of of a Mo target), a quasi monochromatic form of sample excitation can be realized. By interchanging the target (and matching filter), different element ranges can be excited optimally. For example, to obtain the best conditions for determination of trace concentrations of the elements Rb-Nb in geological samples, a Rh secondary target may be selected while for optimal detection of Cr in the same material, a Cu target would be more beneficial.
The ability to simultaneously measure a wide range of elements is one of the greatest advantages of EDXRF. This advantage is strongly reduced when the count rate limitation of the ED detection electronics is taken into consideration. This is due to simultaneous recording of the entire primary source radiation scattered on the specimen and is especially true for examinations on samples with light matrices.

The stationary arrangement of components used in energy-dispersive x-ray fluorescence (EDXRF) is ideally suited for geometrical configurations that exploit polarization phenomena to reduce background and thereby improve signal-to-noise ratios.

Fig. 3.19c shows a configuration employed to achieve a reduction in the background level of EDXRF spectra obtained in direct excitation conditions. In this case, one or more energy bands of the tube emission spectrum are scattered and/or diffracted under (nearly) 90° by means of a suitable scatterer material and/or diffraction crystal. Because scattering rather than fluorescence is used to ‘reflect’ the primary tube spectrum onto the sample, the X-ray beam that impinges on the sample is linearly polarized in the plane.
perpendicular to the tube-scatterer-sample plane. When the Si(Li) detector is also positioned in the former plane at 90° relative to the scatterer-sample axis, the lowest background level will be recorded. The reason for this background reduction is that the polarized photons will preferentially be scattered out of the plane of polarization and therefore will not reach the detector. The optimal geometrical configuration is therefore that tube, scatterer, sample and detector are arranged in an XYZ (also called ‘Cartesian’) geometry, as shown in Fig. 3.19c. For polarization of medium-to-hard radiation \( E > 10 \text{ keV} \) by Barkla-scattering, fairly thick slabs of low-Z materials such as \( \text{Al}_2\text{O}_3 \), \( \text{B}_4\text{C} \) and \( \text{B}_3\text{N} \) are suitable materials. For polarization of softer radiation, the above-mentioned materials are not suitable since for \( E < 10 \text{ keV} \), photo-electric absorption dominates over scattering. In the region 1-10 keV, radiation can be polarized through Bragg diffraction over \( 2\theta \approx 90° \) by using a suitable crystal. For example, HOPG (Highly Oriented Pyrolithic Graphite) is an excellent Bragg polarizer for the (002) reflection of the Rh-L\( _\alpha \) radiation \( (\theta = 43.2°) \). Multiple layer scatterers, for example consisting of a thin layer of HOPG glued on top of an \( \text{Al}_2\text{O}_3 \) substrate, in combination with a Rh tube are useful to determine a wide range of elements simultaneously with good detection limits and sensitivities.

In Fig. 3.20, the spectra are compared that result from direct excitation, secondary excitation and polarized direct excitation of a standard oil sample, containing 21 elements at the 30 µg/g level. The relative detection limits obtained from the three spectra are summarized in Table 3.6; they indicate that the DL values by means of polarized excitation are on average 5 times better than those determined with direct excitation. The secondary target results are factor 2.5 better than the polarized excitation values for elements efficiently excited by the Mo-K\( _\alpha \) line (e.g. Pb); however, elements such as Sn and Cd cannot be determined with the Mo secondary target while they are well excited by the polarized \textit{bremsstrahlung} radiation.
Fig. 3.20. Comparison of EDXRF spectra of an oil standard containing 21 elements (e.g. Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Ba and Pb) with concentrations of 30 µg/g. The spectra (log. scale) are (top) non-polarized, direct excitation by radiation from rhodium anode x-ray tube; (middle) molybdenum secondary excitation; (bottom) polarized excitation by scatter from a HOPG/Al₂O₃ target. 200s measuring time; Rh-end window X-ray tube.

Table 3.6. Limits of detection (LD) (n.d. = not detectable), for some elements in base oil using direct excitation, monochromatic excitation using a Mo secondary target and direct excitation with linearly polarized x-rays (175 W for a measuring time of 200 s and a incident pulse density of about 60,000 cps).

<table>
<thead>
<tr>
<th>element</th>
<th>Limits of Detection, in µg/g</th>
<th>direct excitation</th>
<th>Mo-secondary target</th>
<th>polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>13</td>
<td>8.8</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>3.8</td>
<td>2.9</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>3.1</td>
<td>2</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>2.6</td>
<td>1.2</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>1.7</td>
<td>0.31</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>1.7</td>
<td>0.3</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>2.3</td>
<td>n.d.</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>18.0&quot;</td>
<td>n.d.</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>12</td>
<td>n.d.</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>3.9</td>
<td>0.31</td>
<td>0.79</td>
<td></td>
</tr>
</tbody>
</table>
3.3.5 Radioisotope XRF

Next to EDXRF spectrometers that are intended for use in the laboratory, also a number of portable EDXRF instruments are available. These devices are used in various fields for on-site analysis of works of art, environmental samples, forensic medicine, industrial products and waste materials etc. In its simplest form, the instruments consist of one or more radio-isotope sources combined with a scintillation or gas proportional counter. However, also combinations of radio-sources with thermoelectronically cooled solid-state detectors are available in compact and light-weight packages (below 1 kg). In Fig. 3.21, schematics of various types of radio-source based EDXRF spectrometers are shown. In Fig 21a, the X-rays source is present in the form of a ring; radiation from the ring irradiates the sample from below while the fluorescent radiation is efficiently detected by a solid-state detector positioned at the central axis. Shielding prevents radiation from the source to enter the detector. In Figs. 21bc, the X-ray source has another shape, requiring a different type of shielding. Next to equipment using radio-isotopes as X-ray source, portable equipment that includes miniature low power X-ray tubes is also available; in such devices, almost exclusively the direct excitation form of EDXRF is employed.

Fig. 3.21. Radioisotope-excited X-ray fluorescence analysis by means of (a) an annular source, (b) a central source and (c) a side-looking source.
3.3.6 Total reflection XRF

When X-rays impinge upon an (optically) flat material under a very small angle (typically a few mrad), i.e. nearly grazing the surface, total external reflection occurs. This means that instead of penetrating the material, the X-ray photons will only interact with the top few nm of the material and then be reflected. Material that is present on top of the reflecting surface will be irradiated in the normal manner, and will interact with both the primary and the reflected X-rays. The major difference between conventional EDXRF and TXRF therefore is the excitation geometry. In the standard case of EDXRF the angle between the primary incident radiation and the sample is 45° while the detector is placed normal to the incident beam so that the angle between sample and detector is also 45°. The principle set-up of TXRF is shown in Figure 3.22. A narrow almost parallel beam impinges at angles below the critical angle on the surface of the reflector that carries the sample as randomly distributed micro crystals in the center part of its surface. Since the X-rays scarcely penetrate the reflector, the contribution from scattered primary radiation from the substrate is minimized. As a result of the double excitation of the sample by both the primary and the reflected beam, the fluorescent signal is practically twice as intense as in the standard EDXRF excitation mode. The largest angle at which total external reflection still takes place is called the critical angle of total reflection $\phi_{\text{crit}}$. The critical angles are in the range of a few milliradians for typical reflector materials such as quartz or Si and primary radiation of 9.4 keV (from a W-L tube) or 17.5 keV (from a Mo-anode X-ray tube). With higher energies in the exciting spectrum, adjustments must be made for the proper incident angle below the critical angle, which is given by:

$$\phi_{\text{crit}} \text{ (mrad)} = \frac{20.7}{E \text{ (keV)}} \rho^{1/2} \text{ (g/cm}^3)$$  \hspace{1cm} (18)

The main advantages of TXRF are:
(a) The background caused by scattering of the primary radiation on the substrate is reduced.
(b) The fluorescence intensity is doubled as the primary and reflected beams pass through the sample giving efficient excitation.
(c) The distance between the sample on the reflector surface and the detector can be made small, thus the solid angle for detection is large.
(d) All these advantages lead to lower limits of detection (LD) compared to the standard EDXRF mode.

Depending on the X-ray source and the spectral modification devices, the LD are in the pg range for 2–3-kW X-ray tubes and in the fg range with excitation by means of synchrotron radiation. Fig. 3.15 shows a typical TXRF spectrum; the absolute detection limit values of typical TXRF instruments are shown in Fig. 3.10. Thus, TXRF permit to simultaneously determine trace elements in samples of small volume. Additional advantages are insensitivity to matrix effects, easy calibration, fast analysis times and low costs. In practice, the method is in particular applied for multi-element determinations in water samples of various nature and for the routine analysis of Si-wafer surfaces employed in the micro-electronics industry.

Fig. 3.22. Schematic layout of a TXRF spectrometer.
3.3.7 Microscopic XRF

The basic measuring strategy of microscopic X-ray fluorescence analysis (µ-XRF) is illustrated in Fig 23. This microanalytical variant of bulk EDXRF is based on the localized excitation and analysis of a microscopically small area on the surface of a larger sample, providing information on the lateral distribution of major, minor and trace elements in the material under study. Essentially, a beam of primary X-rays with (microscopically) small cross-section irradiates the sample and induces the emission of fluorescent X-rays from a micro-spot. A suitable detector system collects the fluorescent radiation that carries information on the local composition of the sample. When the sample is moved either manually or under computer control in the X-ray beam path, either spot analyses, line-analysis or image collection is possible.

The difficulties in the exploitation of this method reside with the production of sufficiently intense X-ray beams to allow sensitive micro analysis. Techniques to do this have only recently appeared; in the past, X-rays were considered to be notably difficult to focus to a small dimension beam. Any variants on the basic mode of operation either reside with the method employed for X-ray beam concentration/focussing or with the source type employed: conventional X-ray tubes or synchrotron radiation sources. Especially the increased performance of compact and relatively inexpensive X-ray focusing devices and in particular the development of (poly)capillary X-ray focusing optics, permitting X-ray beams to be focused to below 10 µm diameter spots, has made the development of µ-XRF possible. When used in combination with X-ray tubes, absolute detection limits in the pg area are obtained for thin samples. In massive samples, relative LD values around 10 ppm have been reported. At synchrotron facilities, the capabilities of the µ-XRF method (both regarding spot sizes and detection limits) are significantly better: fg to ag-level absolute detection limits are obtained with beams that are between 0.5-2 µm in diameter. By the use of monochromatic beams of polarized radiation, optimal peak-to-background ratios in the resulting
EDXRF spectra can be obtained, resulting in relative LD levels in the 10-100 ppb range in biological materials. As an example, Fig. 3.24 shows the LD values obtained within 1000 sec by using 14 and 21 keV synchrotron microbeams (of 2 x 15 µm² diameter) to irradiate NIST SRM 1577 Bovine Liver. The application of µ-XRF to a great variety of problems and materials has been described, including geochemistry, archaeology, industrial problems and environmental studies. Especially the fact that quantitative data on (trace) constituents can be obtained at the microscopic level without sample damage is of use in many different circumstances.

Fig 3.23. Principle of µ-XRF.

Fig 3.24. Relative LD values obtained by irradiation of NIST SRM 1577 Bovine Liver by means of 14.4 and 21 keV synchrotron microbeams and Si(Li) or HPGe detectors.
3.4 Matrix effects

3.4.1 Thin and thick samples

The simple linear relation between observed count rate \( R_i \) of analyte element \( i \) and its concentration \( c_i \) shown in Eq. 9 is only valid in a limited number of cases. In general, for monochromatic forms of excitation (with energy \( E_0 \)) and in the absence of enhancement phenomena, the observed XRF count rate \( R_i \) of an element \( i \) (with energy \( E_i \)) is related to the sample thickness \( d \) and its concentration \( c_i \) is the following manner (see also Eq. 34-36):

\[
R_i = S_i c_i \frac{1 - e^{-\chi(E_o, E_i, \rho d)}}{\chi(E_o, E_i, \rho d)} = S_i c_i A_i \quad \text{with} \quad \chi(E_o, E_i) = \mu(E_o) \csc \alpha + \mu(E_i) \csc \beta
\]

(19)

where \( \alpha \) and \( \beta \) are the angles under which the X-rays impinge and take-off relative to the sample surface (see Fig. 3.25) and \( \rho \) is the sample density. The absorption factor \( A_i \) is obtained by adding all contributions to \( R_i \) produced in a series of infinitesimal sample volumes at various depths \( z \) inside the sample and by considering an attenuation factor \( \exp[-\mu(E_o) \rho z \csc \alpha] \) for the primary radiation while penetrating into the sample until this depth and an attenuation factor \( \exp[-\mu(E_i) z \csc \beta] \) for the fluorescent radiation when emerging from the sample towards the detector. When polychromatic forms of excitation are used, Eq. 19 is more complicated and involves an integral over the intensity distribution of the X-ray source (see below, Eq. 36).

Fig. 3.25. Basic XRF irradiation geometry.

Detector

\( \alpha \)

\( \beta \)

\( A \)

\( d \)

\( z \)
As a result of the attenuation of both primary and fluorescent radiation within the sample, there is a critical depth in the sample $d_{\text{thick}}$ below the surface, beyond which any emitted photon is essentially absorbed and therefore will not make a significant contribution to the detected fluorescent intensity. This critical penetration depth varies as a function of matrix composition and is also strongly dependent on the energy of the (primary and) fluorescent radiation. Sample that have a thickness greater than the critical penetration depth for a specific kind of fluorescent radiation are sometimes referred to as ‘infinitely thick’ or ‘massive’ samples. In Table 3.7 values for $d_{\text{thick}}$ in a geological (a silicate rock) and metallurgical (steel) matrix are listed for various fluorescent line energies. For low-energy photons (e.g., the $K_\alpha$-photons of low-Z elements such as Al or Na), the critical penetration depth is very small (a fractional to a few $\mu$m) so that compositional information that exclusively pertains to the surface layers of the sample is obtained. When more penetrating fluorescent radiation is used (e.g. Rb-$K_\alpha$ at 13.39 keV), having $d_{\text{thick}}$ values of several mm, compositional information from much deeper in the sample is obtained.

In many practical situations, it is important to ensure that the sample presented for analysis is sufficiently thick (i.e. thicker than the highest critical penetration depth among the various fluorescent signals being used), so that the observed analytical signals no longer depend on sample thickness but only on analyte concentration.

Next to the critical penetration depth $d_{\text{thick}}$, it is also useful to define a critical thickness $d_{\text{thin}}$ below which absorption and enhancement effects can be neglected. For analysis of such ‘thin-film’ samples, the calibration relations of Eq. 8 and 9 are valid and matrix effect corrections need not be applied. By convention, $d_{\text{thin}}$ corresponds to the situation where the total attenuation in the sample is equal to 1%. Table 3.7 lists typical $d_{\text{thin}}$ values for various fluorescent line energies in two matrices.
Table 3.7. Critical penetration depth and thin film thickness of various fluorescent lines in two matrices. [Adapted from P. Potts, “Handbook of Silicate Rock Analysis”, 1987, Glasgow, Blackie].

<table>
<thead>
<tr>
<th>Element</th>
<th>Energy/wavelength of $K_{\alpha}$ line $E$, keV</th>
<th>l, nm</th>
<th>Excitation spectrum tube anode</th>
<th>Critical Penetration Depth $d_{\text{thick}}$ (mm)</th>
<th>Thin film thickness $d_{\text{thin}}$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{\text{keV}}$</td>
<td>$l_{\text{nm}}$</td>
<td>Cr</td>
<td>Silicate</td>
<td>Steel</td>
</tr>
<tr>
<td>C</td>
<td>0.28</td>
<td>4.4</td>
<td>Cr</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>Na</td>
<td>1.04</td>
<td>1.19</td>
<td>Cr</td>
<td>4.8</td>
<td>0.4</td>
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<td>0.713</td>
<td>Cr</td>
<td>13</td>
<td>1.6</td>
</tr>
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<td>Cr</td>
<td>36</td>
<td>9.6</td>
</tr>
<tr>
<td>Cr</td>
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<td>0.229</td>
<td>Rh</td>
<td>90</td>
<td>30</td>
</tr>
<tr>
<td>Fe</td>
<td>6.43</td>
<td>0.194</td>
<td>Rh</td>
<td>180</td>
<td>43</td>
</tr>
<tr>
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<td>0.0927</td>
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<td>Rh</td>
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<td>62</td>
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<tr>
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<td>W</td>
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</tr>
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<td>33.44</td>
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<td>W</td>
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<td>0.0301</td>
<td>W</td>
<td>15400</td>
<td>886</td>
</tr>
</tbody>
</table>

3.4.2 Primary and secondary absorption, direct and third element enhancement

In the context of X-ray fluorescence analysis, matrix effects are caused by attenuation and enhancement phenomena that influence the intensity of the fluorescent X-ray lines observed from a sample. As the magnitude of the matrix effects varies with elemental composition, the observed XRF intensity is no longer linearly proportional to the concentration of the analyte (Eq. 9). Corrections must therefore be applied to the measured intensity data to account for:

a) primary absorption (see Fig. 3.26a): this occurs because all atoms of the specimen matrix will absorb photons from the primary source. Since there is competition for these primary photons by the atoms making up the specimen, the intensity/wavelength distribution of these photons available for the excitation of a given analyte element may be modified by other matrix elements. In this manner, the intensity and spectral distribution of the X-ray flux available to excite the sample atoms can change with penetration depth. This phenomenon is known as ‘beam hardening’;
b) *secondary absorption*: this refers to the effect of the absorption of characteristic analyte radiation by the specimen matrix. As characteristic radiation passes out from the specimen in which it was generated, it will be absorbed by all matrix elements, by amounts relative to the mass absorption coefficients of these elements.

![Diagram](image)

Fig 26. Primary excitation versus two-element and three-element enhancement.

c) *direct (or second-element) enhancement* (see Fig. 3.26b): in situations where the energy of a fluorescent photon (e.g., Ni-K$_\alpha$ at 7.47 keV) is immediately above the absorption edge of a second element (e.g., the K-edge of Fe at 7.11 keV), the fluorescence intensity of the second element (here: Fe-K$_\alpha$ and Fe-K$_\beta$ radiation) will be enhanced as a result of the preferential excitation (here: by Ni-K$_\alpha$ radiation) within the sample. The magnitude of this effect is not always significant but is readily observable in alloys of specific combinations of elements (e.g., Cr-Fe-Ni steels) and in multiplayer thin film samples.
d) indirect (or third-element) enhancement (see Fig. 3.26c): For example in a stainless steel matrix, the observed intensity of the Cr-K characteristic radiation (Cr-K absorption edge at 5.99 keV) is enhanced by secondary excitation due to Fe-K ($K_{\alpha}$ at 6.40 keV) and Ni-K radiation. Since the intensity of the Fe-K radiation is itself enhanced (see above), part of the Cr enhancement due to Fe is a tertiary effect originating from Ni.

3.5 Data treatment

The process to convert experimental XRF data into analytically useful information (usually in the form of concentration values of elemental constituents whose X-ray peaks are visible above the background in the spectrum) can be divided into two steps: first the evaluation of the spectral data, whereby the net height or the net intensity of the X-ray peaks is determined, taking care to correct for peak overlap (if any) between X-ray lines of different elements and secondly the conversion of the net X-ray intensities into concentration data, i.e. the quantification. In this last step, especially, the appropriate correction of matrix effects is a critical issue.

3.5.1 Counting statistics

The production of X-rays is a random process that can be described by a Gaussian distribution. Since the number of photons counted is nearly always large, typically thousands of hundreds or thousands, rather than a few hundred, the properties of the Gaussian distribution can be used to predict the probable error for a given count measurement. There will be a random error $s_{I}$ associated with a measured intensity value $I$, this being equal to $I^{1/2}$. As an example, if $10^6$ counts are taken, the 1s standard deviation will be $[10^6]^{1/2} = 10^3$, or 0.1%. The measured parameter in wavelength-dispersive X-ray spectrometry is generally the counting rate $R=I/t$ and, based on what has been already stated, the magnitude of the relative random counting error $\text{RSD}(R)$ associated with a given measured rate $R$ can be expressed as:
\[
RSD(R) (\%) = 100\% \frac{s_R}{R} = 100\% \frac{s_I}{I} = 100\% \frac{\sqrt{I}}{I} = \frac{100\%}{\sqrt{R}}
\]  

(20)

Care must be exercised in relating the counting error (or indeed any intensity related error) with an estimate of the error in terms of concentration. Provided that the sensitivity of the spectrometer in counts per second per percent, is linear, a count error can be directly related to a concentration error. However, where the sensitivity of the spectrometer changes over the range of measured response, a given fractional count error may be much greater when expressed in terms of concentration.

3.5.2 Spectrum evaluation techniques

Spectrum evaluation is a crucial step in X-ray analysis, as much as sample preparation and quantification. As with any analytical procedure, the final performance of X-ray analysis is determined by the weakest step in the process. Spectrum evaluation in EDXRF analysis is more critical than in WDXRF spectrometry because of the relatively low resolution of the solid-state detectors employed.

In general, it is possible to distinguish between amplitude and energy noise in (ED)X-ray spectra. Amplitude noise is the result of the statistical nature of the counting process in which random events (the arrival of X-ray photons in the detector) are observed during a finite time interval. Poisson statistics cause the typical channel-to-channel fluctuations observed in X-ray spectra. Energy noise, on the other hand, causes the characteristic X-ray lines in EDXRF spectra to appear much wider (of the order of 120-150 eV) than their natural line widths (typically 5-10 eV). It results partly from the photon-to-charge conversion process in the detector and partly from the electronic noise that is introduced in the amplification and processing steps that follow it. Accordingly, characteristic X-ray lines appear as nearly Gaussian peaks in EDXRF spectra.
In WDXRF spectra, where at least one of these noise contributions usually is absent (the noise in the energy/wavelength dimension is significantly lower as a result of the much higher resolution of the dispersion systems used), spectrum evaluation in principle, is much more simple and sometimes can be discarded with altogether. Because the X-ray lines appear as narrow, well-defined peaks, their net X-ray intensities and that of the background in the same region can be determined with great accuracy. The few cases of peak overlap (e.g., between As-K$_\alpha$ and Pb-L$_\alpha$, where the separation of 8 eV is less than the natural line width of As-K$_\alpha$) can be dealt with on a case-by-case basis or avoided by the use of another, non-overlapped, X-ray line of the elements involved as analytical signals (e.g., the As-K$_\beta$ line).

In both WDXRF and EDXRF, the net number of counts under a characteristic X-ray line (i.e., the integrated peak intensity) is proportional to the concentration of the analyte. At constant resolution, this proportionality also exists between concentration and net peak height. In EDXRF (where the detector resolution is low and changes considerably with energy and many peaks are low in intensity), the use of the net peak area as analytical signal is preferred, since this also results in a lower statistical uncertainty for the small peaks. In WDXRF (where the detector resolution is high and must less dependent on the wavelength, while often sharp and intense peaks are encountered), the acquisition of the entire peak profile is often too time consuming so that the count rate is frequently measured only at the peak maximum.

3.5.3 Data extraction in WDXRF.

In WDXRF, most often the count rate $R_{\text{max}}$ at the angle of the peak maximum, corrected for background is used as analytical signal. In order to estimate the appropriate background below the line, the background count rate at slightly lower and higher 20-values is measured and the average calculated. If $T$ is the number of counts accumulated during a time interval $t_T$ at the top of the peak
and $B$ is the corresponding background counts (during a time $t_B$), the net count rate $R$ is given by the difference of the total and background count rates $R_T$ and $R_B$:

$$R = R_T - R_B = \frac{T}{t_T} - \frac{B}{t_B}$$

(21a)

and, considering that $s^2_T = T$ and $s^2_B = B$, the uncertainty $s_R$ on the net count rate $R$ is given by:

$$s_R^2 = \frac{T}{t_T^2} + \frac{B}{t_B^2} = \frac{R_T}{t_T} + \frac{R_B}{t_B}$$

(21b)

Accordingly, in WDXRF, several counting strategies may be employed to keep this number as low as possible. In the ‘optimum fixed time’ strategy, the minimum uncertainty is obtained within a time interval $t = t_T + t_B$ when $t_T$ and $t_B$ are chosen in such a way that:

$$\frac{t_T^2}{t_B^2} = \frac{R_T}{R_B}$$

(22)

In this case, the uncertainty $s_R$ can be written as:

$$s_R = \frac{\sqrt{R_T} + \sqrt{R_B}}{\sqrt{t}}$$

(23)

**Data extraction in EDXRF – simple case: no peak overlap.** The most straightforward method to obtain the net area of an isolated, non-overlapped peak in an EDXRF spectrum is to interpolate the background under the peak and to sum the net channel contents in a window enclosing the peak. Thus, the net peak area $N$ is given by:

$$N = \sum_i [y_i - y_B(j)] = \sum_i y_i - \sum_i y_B(j) = T - B$$

(24)
where the summation runs over the spectral window (containing $n_T$ channels) under consideration. Thus, the uncertainty $s_N$ can be written as:

$$s^2_N = s^2_T + s^2_B = T + B \tag{25}$$

The background height $y_B(j)$ in channel $j$ of the peak window can be interpolated between the average background height left and right of the peak (resp. $y_{B,L} = B_L/n_L$ and $y_{B,R} = B_R/n_R$ where $B_L$ and $B_R$ are the integrals of the left and right background windows and $n_L$, $n_R$ their widths in channels) (see Fig. 3.27):

$$y_B(j) = y_{B,L} + \frac{y_{B,R} - y_{B,L}}{j_{B,R} - j_{B,L}} \cdot (j - j_{B,L}) \tag{26}$$

where $j_{B,L}$ and $j_{B,R}$ represent the channels between which the background is linearly interpolated. When both background windows around the peak have equal width (i.e., $n_L = n_R = n_B/2$ channels) and are positioned symmetrically around the maximum, the uncertainty on $N$ is given by:

$$s^2_N = T + (n^2_T/n^2_B) \cdot (B_L + B_R) \tag{27}$$

Fig. 3.27. Background estimation below an isolated photo peak.
3.5.4 Data extraction in EDXRF – multiple peak overlap.

The above-described simple integration procedure is very useful for explorative data analysis but implicitly assumes that within the energy window used, a single, non-overlapped peak is present with a high peak-to-background ratio. In general, these assumptions are not valid: peak overlap frequently occurs in energy-dispersive X-ray spectra while, especially for peaks corresponding to trace constituents, the background intensity below the peak may be of the same order or larger than the net peak intensity. In these cases, the use of too simple spectrum evaluation procedures may negate all the efforts that are made both during the data collection and during the further quantitative processing of the data to increase the reliability of the final (trace) element concentrations. An established way of proceeding is to use a non-linear least squares strategy to minimize the weighted difference \( \chi^2 \) between the experimental data \( y_i \) and a mathematical fitting function \( y_{\text{fit}}(i) \):

\[
\chi^2 = \frac{1}{n-m} \sum_i \left( \frac{(y_i - y_{\text{fit}}(i))^2}{y_i} \right)
\]

(28)

where \( y_i \) is the observed content of channel \( i \) in the spectrum being processed and \( y_{\text{fit}}(i) \) is the calculated fitting function in this channel. \( n \) is the total number of channels in the fitting window while \( m \) represents the number of parameters in the fitting function. The latter consists of two parts, describing respectively the spectral background and the photo peaks:

\[
y_{\text{fit}}(i) = y_{\text{back}}(i) + y_{\text{peak}}(i) = y_{\text{back}}(i) + \sum_j y_j(i)
\]

(29)

where the index \( j \) runs over all characteristic line groups which appear in the spectrum. For each line group \( j \) (e.g., Fe-K, Pb-L3), the contribution \( y_j(i) \) to the \( i \)th channel is calculated as:

\[
y_j(i) = A_j \left( \sum_{k=1}^{N_j} r_{jk} G(E_{jk}, i)t(E_{jk}) \right)
\]

(30)

where \( A_j \) represents the total area of all photo peaks in line group \( j \) (comprised, e.g., of the Fe-K\textsubscript{\textgamma} and -K\textsubscript{\times} lines); these are optimizable parameters during the least squares fitting process. The index \( k \) runs over all lines in
group \( j \), each line having a relative abundance \( r_{jk} \) (with \( \Gamma_k r_{jk} = 1 \)). \( G_{jk} \) represents a gaussian function centered around \( E_{jk} \); \( t(E_{jk}) \) denotes the total attenuation factor for X-rays with energy \( E_{jk} \) as defined by the absorption of radiation in the detector, in absorbers placed between sample and detector and in the sample itself. This model can also be expanded to account for spectral artifacts that are generated in the solid-state detector. In Fig. 3.28, the result of non-linear deconvolution of the complex multiplets constituted by the W-L\(_1\), L\(_2\) and L\(_3\)-lines is shown.

![Spectral deconvolution in case of complex multiplets.](image)

Fig. 3.28. Spectral deconvolution in case of complex multiplets.

The background in ED-XRF spectra is the result of many processes and therefore can have a fairly complex shape. Although it is not impossible to calculate/predict this shape, during spectrum evaluation, usually a more empirical (and faster) approach is favored. Either the background shape is estimated \textit{a priori} so that it can be subtracted from the experimental data before the actual fitting (‘background estimation’) or it is described by a suitable mathematical function (usually a polynomial of some kind), of which
the coefficients are optimized together with the other parameters of the fitting model (‘background modeling’).

3.5.5 Quantitative calibration procedures

In the X-ray analytical laboratory the quantitative method of analysis employed will be typically determined by a number of circumstances of which probably the four most common are: the complexity of the analytical problem; the time allowable; the data processing and calibration software present and the number of standards available. It is convenient to break quantitative analytical methods down into two major categories: single-element methods and multiple-element methods.

Single Element Methods
- Internal standardization
- Standard addition

Multiple Element Methods
- Type standardization
- Use of influence coefficients
- Fundamental parameter techniques

The simplest quantitative analysis situation to handle is the determination of a single element in a known matrix. A slightly more difficult case might be the determination of a single element where the matrix is unknown. As shown in the table, three basic methods are commonly employed in this situation: use of internal standards, use of standard addition, or use of a scattered line from the X-ray source.

The most complex case is the analysis of all, or most, of the elements in a sample about which little or nothing is known. In this case a full qualitative analysis would be required before any attempt is made to quantify the matrix elements. Once the qualitative composition of the sample is known, again, one of three general techniques is typically applied: use of type
standardization, use of an influence coefficient method, or use of a fundamental parameter technique. Both the influence coefficient and fundamental parameter technique require a computer for their application.

The correlation between the characteristic count rate $R_i$ of an analyte element and the concentration $c_i$ of that element is typically nonlinear over wide ranges of concentration, due to inter-element effects between the analyte element and other elements making up the specimen matrix. However, the situation can be greatly simplified in the case of homogeneous specimens, where severe enhancement effects are absent, and here, the slope of a calibration curve $S_i$ is inversely proportional to the total absorption factor $A_i$ of the specimen for the analyte wavelength:

$$S_i = \frac{R_i}{c_i A_i^{-1}}$$  \hspace{1cm} (31)

As an example, the data in Table 3.8 show how the net intensity of the Fe-K$_\alpha$ line (Fe K-L$_{3,2}$ transition) resulting from a concentration of 1% iron strongly depends on the matrix composition: the Fe-intensity obtained from a graphite sample, in which virtually no absorption takes place ($A \approx 1$) of the Fe-K$_\alpha$ radiation is ca. 600 times higher than that obtained from the same Fe concentration in a strongly absorbing lead sample. With the Ni sample, a higher intensity than in the Cr sample observed, even though the absorption in the Ni matrix is higher. This is caused by the enhancement effect due to the Ni characteristic X-rays that additionally excite the Fe atoms. The combination of matrix absorption and enhancement effects causes the calibration curves in XRF to be nonlinear. Fig. 3.29 shows calibration curves for Pb and Sn in binary Pb-Sn alloys. Different quantitative analysis schemes are used depending on the type of matrix, the concentration range and the availability of the standards.
Table 3.8. Count rate (in cps) of the Fe-K\textsubscript{\alpha} line obtained from a 1% concentration of Fe in various matrices.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1200</td>
</tr>
<tr>
<td>Al</td>
<td>108</td>
</tr>
<tr>
<td>Cr</td>
<td>22</td>
</tr>
<tr>
<td>Ni</td>
<td>79</td>
</tr>
<tr>
<td>Pb</td>
<td>20</td>
</tr>
</tbody>
</table>

Fig. 3.29 Calibration curves for Pb-L\textsubscript{\alpha}, Sn-K\textsubscript{\alpha} and Sn-L\textsubscript{\alpha} in Pb-Sn binaries. The Pb-L\textsubscript{\alpha} intensity shows a slight enhancement effect (due to the Sn-K lines); the Sn-K\textsubscript{\alpha} and Sn-L\textsubscript{\alpha} curves indicate different degrees of absorption in the sample. In case of Sn-L\textsubscript{\alpha}, the absorption effect apparently dominates over the enhancement of the Sn-L\textsubscript{\alpha} intensity by both the Pb-L and Sn-K lines.

a. Single element techniques

Single-element techniques reduce the influence of the absorption term \(\mu\) in Equation (30), generally by referring the intensity of the analyte wavelength to a similar wavelength, arising either from an added standard or from a
scattered line from the X-ray tube. In certain cases, limiting the concentration range of the analyte may allow the assumption to be made that the absorption value does not significantly change over the concentration range and the calibration curve is essentially linear.

Thin film approach. Quantitative analysis of thin films, such as filters loaded with aerosol particles, can be done by simply comparing the count rate for a particular element in the sample with the count rate observed in a thin film standard, because matrix effects are virtually absent. Special reference standards may be made up for particular purposes, and these may serve the dual purpose of instrument calibration as well as establishing working curves for analysis. As an example, two thin glass film standard reference materials (SRMs) specially designed for calibration of X-ray spectrometers are available from the National Institute of Standards and Technology in Washington as SRMs 1832 and 1833. They consist of a silica-based film deposited by focused ion-beam coating onto a polycarbonate substrate. SRM 1832 contains aluminum, silicon, calcium, vanadium, manganese, cobalt and copper, and SRM 1833 contains silicon, potassium, titanium, iron and zinc.

Internal standardization. One of the most useful techniques for the determination of a single analyte element in a known or unknown matrix is to use an internal standard. The technique is one of the oldest methods of quantitative analysis and is based on the addition of a known concentration of an element that features an X-ray line with a wavelength/energy close to that of the analyte wavelength. The assumption is made that the effect of the matrix on the internal standard is essentially the same as the effect of the matrix on the analyte element. Internal standards are best suited for the measurement of analyte concentrations below ca 10%. The reason for this limit arises because it is generally advisable to add the internal standard element at about the same concentration level as that of the analyte. When more than 10% of the internal standard is added, it may significantly change
the specimen matrix and introduce errors into the determination. Care must also be taken to ensure that the particle sizes of specimen and internal standard are about the same, and that the two components are adequately mixed. Where an appropriate internal standard cannot be found it may be possible to use the analyte itself as an internal standard. This method is a special case of standard addition (spiking).

*Type standardization.* Provided that the total specimen absorption does not vary significantly over a range of analyte concentrations, and provided that enhancement effects are absent and that the specimen is homogeneous, a linear relationship will be obtained between analyte concentration and measured characteristic line intensity. Where these provisos are met, type standardization techniques can be employed.

In this way, linear calibration curves can be used to determine trace and minor element concentrations in alloys, mineral pellets and liquids provided that the major element concentrations of standards and unknowns are very similar. In this case, the matrix effect remains the same.

It will also be clear from previous discussion that by limiting the range of analyte concentrations to be covered in a given calibration procedure, the range in absorption can also be reduced. Type standardization is probably the oldest of the quantitative analytical methods employed, and the method is usually evaluated by taking data from a well-characterized set of standards, and, by inspection, establishing whether a linear relationship is indeed observed. Where this is not the case, the analyte concentration range may be further restricted. The analyst of today is fortunate in that many hundreds of good reference standards are commercially available. While the type standardization method is not without its pitfalls, it is nevertheless extremely useful and is especially useful for quality control type applications where a finished product is being compared with a desired product.
b. Multiple element techniques

To determine major and minor elements in complex samples, more elaborate matrix correction algorithms need to be applied. They can be roughly divided into two categories: the influence coefficient and the fundamental parameter method.

*Influence coefficient methods.* All these models have essentially the same form:

\[
\frac{c_i}{R'_i} = K_i + \text{model-dependent term(s)}
\]  

(32)

describing the (empirical) relation between an analyte concentration \(c_i\), its X-ray intensity ratio \(R'_i\), an instrument-dependent term \(K_i\) that is equal to the inverse of the sensitivity of the spectrometer for the analyte in question \((K_i = 1/S_i)\), and a term that corrects this sensitivity term for the effect of the matrix. \(R'_i\) is the ratio of the analyte intensity in the unknown sample to that obtained from a pure element standard, measured under identical circumstances. The different methods only vary in the form of the correction term. Below, the relations used by some of the commonly employed influence methods are listed:

- **Linear model**  
  \[
  \frac{c_i}{R'_i} = K_i
  \]  
  (33a)

- **Lachance-Traill**  
  \[
  \frac{c_i}{R'_i} = K_i + \sum_j \alpha_{ij} c_j
  \]  
  (33b)

- **Claisse-Quintin**  
  \[
  \frac{c_i}{R'_i} = K_i + \sum_j \alpha_{ij} c_j + \sum_j \gamma_{ij} c_j^2
  \]  
  (33c)

- **Rasberry-Heinrich**  
  \[
  \frac{c_i}{R'_i} = K_i + \sum_j \alpha_{ij} c_j + \sum_{k\neq j} \beta_{ijk} \frac{c_k}{1 + c_i}
  \]  
  (33d)

- **Lachance-Claisse**  
  \[
  \frac{c_i}{R'_i} = K_i + \sum_j \alpha_{ij} c_j + \sum_j \sum_{k>j} \alpha_{ijk} c_j c_k
  \]  
  (33e)

where all concentrations are expressed as mass fractions.
All the models are concentration correction models in which the product of the influence coefficient ($\alpha$, $\beta$, or $\gamma$ in the above equations) and the concentration of the interfering element are used to correct the slope of the analyte calibration curve. The Lachance-Traill model is the earliest model; after that, in the Rasberry-Heinrich model, the influence of the absorbing and enhancing elements is separated by the use of resp. the $\alpha$ and $\beta$ coefficients. When the physics of the X-ray excitation are thoroughly studied, it becomes clear that the above-mentioned models are too simple and that all binary coefficients (the $\alpha_{ij}$'s and $\beta_{ij}$'s) systematically are dependent on the composition. Both the Claisse-Quintin and the Lachance-Claisse models use higher order cross-terms to correct for enhancement and third element effects. Accordingly, these models are in general more suited for use in a very wide concentration range.

**Fundamental parameter method.** The fundamental parameter method is based on the physical theory of X-ray production rather than on empirical relations between observed X-ray count rates and concentrations of standard samples. In general, the observed XRF count rate $R_{i,K\alpha}$ of (the $K\alpha$ line of) an element $i$, obtained by polychromatic excitation of a sample with thickness $d$ and density $\rho$, can be written as:

$$R_{i,K\alpha} = \frac{G_1}{\sin \varphi} \int_{E_{abs}}^{E_{max}} \int_0^d I_0(E) \sigma_{i,K\alpha}(E) c_i H_i(E) e^{-z(E,E_{i,K\alpha})} G_2 B(E,E_{i,K\alpha}) \varepsilon(E_{i,K\alpha}) dz dE$$

(34)

where the quantity $\sigma_{i,K\alpha}$ is the effective cross-section for production of $K\alpha$-radiation of element $i$:

$$\sigma_{i,K\alpha}(E) = \tau_{i,K\alpha}(E) \cdot \omega_{i,K} \cdot p_{i,K\alpha}$$

(35)

(with $p_{i,K\alpha}$ the probability of producing a $K\alpha$-fluorescent photon from a vacancy in the K-shell and $\omega_{i,K}$ its fluorescence yield). $E_{abs}$ is the absorption edge energy and $E_{i,K\alpha}$ the $K\alpha$-line energy of element $i$. $I_0(E)dE$ is the spectral...
distribution of the exciting radiation with $E_{\text{max}}$, its maximum energy (see Fig. 3.6), $G_1$ and $G_2$ are geometry constants, $\chi(E,E_{i,K\alpha})$ is defined in Eq. 19. $H_i(E,E_{i,K\alpha})$ is a factor describing secondary and higher order excitation (at low concentrations, $H_i = 1$) while the factor $B(E,E_{i,K\alpha})$ describes the absorption of the radiation in the medium between tube, sample and detector (e.g., air, He). $\epsilon(E_{i,K\alpha})$ is the efficiency of the detector. After integration over the sample depth, Eq. 34 becomes:

$$R_{i,K\alpha} = \int_{E=E_{i,abs}}^{E_{\text{max}}} I_0(E) \frac{G_1 \rho d}{\sin \varphi} \sigma_{i,K\alpha}(E)c_i \times \frac{1-e^{-\chi(E,E_{i,K\alpha})\rho d}}{\chi(E,E_{i,K\alpha})\rho d} \times G_2 B(E,E_{i,K\alpha}) \epsilon(E_{i,K\alpha}) dE$$

(36)

Table 3.9. Analysis of Tool Steels obtained by means of a fundamental parameter program and one calibration standard. Min., max.: minimum and maximum concentrations in the series of analyzed samples. Standard deviation on the basis of the difference between calculated and certified concentrations. [Adapted from Handbook of X-ray Spectrometry, 1st ed., Chapter 5, p. 320].

<table>
<thead>
<tr>
<th>Element</th>
<th>Min (%)</th>
<th>Max (%)</th>
<th>Standard Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.14</td>
<td>0.27</td>
<td>0.03</td>
</tr>
<tr>
<td>S</td>
<td>0.015</td>
<td>0.029</td>
<td>0.003</td>
</tr>
<tr>
<td>P</td>
<td>0.022</td>
<td>0.029</td>
<td>0.003</td>
</tr>
<tr>
<td>Mo</td>
<td>0.2</td>
<td>9.4</td>
<td>0.04</td>
</tr>
<tr>
<td>Mn</td>
<td>0.21</td>
<td>0.41</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr</td>
<td>2.9</td>
<td>5</td>
<td>0.13</td>
</tr>
<tr>
<td>Co</td>
<td>0</td>
<td>10</td>
<td>0.2</td>
</tr>
<tr>
<td>C</td>
<td>0.65</td>
<td>1.02</td>
<td>0.16</td>
</tr>
<tr>
<td>W</td>
<td>1.8</td>
<td>20.4</td>
<td>0.52</td>
</tr>
</tbody>
</table>

The above fundamental parameter equation relates the intensity of one element to the concentration of all elements present in the sample. A set of such equations can be written, one for each element to be determined. This set of equations can only be solved in an iterative way, making the method computationally complex. Moreover, an accurate knowledge of the shape of the excitation spectrum $I_0(E)dE$, of the detector efficiency $\epsilon$ and of the fundamental parameters $\mu$, $\tau$, $\omega$ and $p$ is required. The fundamental parameter method is of interest because it allows for semi-quantitative (5-10% deviation)
analysis of completely unknown samples and is therefore of use in explorative phases of investigations. Several computer programs are available that allow to perform the necessary calculations at various levels of sophistication. As an example, in Table 3.9, the relative standard deviation between certified and calculated concentration of the constituents of series of tool steels are listed.

3.5.6 Error sources in X-ray Fluorescence Analysis

Table 3.10 lists the four main categories of random and systematic error encountered in X-ray fluorescence analysis. The first category includes the selection and preparation of the sample to be analyzed. Two stages are generally involved before the actual prepared specimen is presented to the spectrometer, these being sampling and specimen preparation. The actual sampling is rarely under the control of the spectroscopist and it generally has to be assumed that the container containing the material for analysis does, in fact, contain a representative sample. It will be seen from the table that, in addition to a relatively large random error, inadequate sample preparation and residual sample heterogeneity can lead to very large systematic errors. For accurate analysis these errors must be reduced by use of a suitable specimen preparation method. The second category includes errors arising from the X-ray source previously discussed. Source errors can be reduced to less than 0.1% by the use of the ratio counting technique, provided that high frequency transients are absent. The third category involves the actual counting process and these errors can be both random and systematic. System errors due to detector dead time can be corrected either by use of electronic dead time correctors or by some mathematical approach. The fourth category includes all errors arising from inter-element effects. Each of the effects listed can give large systematic errors that must be controlled by the calibration and correction scheme.
Table 3.10. Sources of Error in X-ray fluorescence analysis

<table>
<thead>
<tr>
<th>Source</th>
<th>Random (%)</th>
<th>Systematic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Sample preparation</td>
<td>0 - 1</td>
<td>0 - 5</td>
</tr>
<tr>
<td>Sample inhomogeneity</td>
<td>-</td>
<td>0 - 50</td>
</tr>
<tr>
<td>2 Excitation source fluctuations</td>
<td>0.05 - 0.2</td>
<td>0.05 - 0.5</td>
</tr>
<tr>
<td>Spectrometer instability</td>
<td>0.05 - 0.1</td>
<td>0.05 - 0.1</td>
</tr>
<tr>
<td>3 Counting statistics</td>
<td>time dependent</td>
<td>-</td>
</tr>
<tr>
<td>Dead time correction</td>
<td>-</td>
<td>0 - 25</td>
</tr>
<tr>
<td>4 Primary absorption</td>
<td>-</td>
<td>0 - 50</td>
</tr>
<tr>
<td>Secondary absorption</td>
<td>-</td>
<td>0 - 25</td>
</tr>
<tr>
<td>Enhancement</td>
<td>-</td>
<td>0 - 15</td>
</tr>
<tr>
<td>Third element effects</td>
<td>-</td>
<td>0 - 2</td>
</tr>
</tbody>
</table>

3.6 Specimen Preparation for X-ray Fluorescence Analysis

Because X-ray spectrometry is essentially a comparative method of analysis, it is vital that all standards and unknowns be presented to the spectrometer in a reproducible and identical manner. Any method of specimen preparation must give specimens which are reproducible and which, for a certain calibration range, have similar physical properties including mass attenuation coefficient, density, particle size, and particle homogeneity. In addition the specimen preparation method must be rapid and cheap and must not introduce extra significant systematic errors, for example, the introduction of trace elements from contaminants in a diluent. Specimen preparation is an all-important factor in the ultimate accuracy of any X-ray determination, and many papers have been published describing a multitude of methods and recipes for sample handling. In general samples fit into three main categories: Samples that can be handled directly following some simple pretreatment such as pelletizing or surfacing. For example, homogeneous samples of powders, bulk metals or liquids.
Samples that require significant pretreatment. For example, heterogeneous samples, samples requiring matrix dilution to overcome inter-element effects and samples exhibiting particle size effects.

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Samples that require special handling treatment. For example, samples of limited size, samples requiring concentration or prior separation and radioactive samples.

The ideal specimen for X-ray fluorescence analysis is one in which the analyzed volume of specimen is representative of the total specimen, which is, itself, representative of the sample submitted for analysis. There are many forms of specimen suitable for X-ray fluorescence analysis, and the form of the sample as received will generally determine the method of pretreatment. It is convenient to refer to the material received for analysis as the sample, and that what actually is analyzed in the spectrometer as the specimen. While the direct analysis of certain materials is certainly possible, more often than not some pretreatment is required to convert the sample to the specimen. This step is referred to as specimen preparation. In general, the analyst would prefer to analyze the sample directly, because if it is taken as received, any problems arising from sample contamination that might occur during pretreatment are avoided. In practice, however, there are three major constraints that may prevent this ideal circumstance from being achieved: sample size, sample size homogeneity and sample composition heterogeneity. Problems of sample size are frequently severe in the case of bulk materials such as metals, large pieces of rock, etc. Problems of sample composition heterogeneity will generally occur under these circumstances as well, and in the analysis of powdered materials heterogeneity must almost always be considered. The sample as received may be either homogeneous or heterogeneous; in the latter case, it may be necessary to render the sample homogeneous before an analysis can be made. Heterogeneous bulk solids are generally the most difficult kind of sample to handle, and it may be necessary to dissolve or chemically react the material in some way to give a homogeneous preparation. Heterogeneous powders are either ground to a fine particle size and then pelletized, or fused with a glass-forming material such as borax. Solid material in liquids or gases must be filtered out and the
filter analyzed as a solid. Where analyte concentrations in liquids or solutions are too high or too low, dilution or preconcentration techniques may be employed to bring the analyte concentration within an acceptable range.

3.7 Advantages and limitations

3.7.1 Qualitative Analysis
Qualitative analysis is in principle very simple with XRF and is based on the accurate measurement of the energy, or wavelength, of the fluorescent lines observed. Since many WD-XRF spectrometers operate sequentially, a $2\theta$ scan needs to be performed. The identification of trace constituents in a sample can sometimes be complicated by the presence of higher order reflections or “satellite” lines from major elements. With energy dispersive XRF, the entire X-ray spectrum is acquired simultaneously. The identification of the peaks, however, is rendered difficult by the comparatively low resolution of the ED detector. In qualitative analysis programs, the process is simplified by overplotting so called “KLM” markers onto an (unknown) spectrum. These markers indicate the theoretical position of the K, L and M lines of a specific element; when these observed peaks coincide with the line markers, an element is positively identified.

3.7.2 Detection limits
For a particular element, the detection limit depends on the sensitivity and on the count rate of the continuum below the peak and is inversely proportional to the measurement time. Detection limits can be improved by increasing the sensitivity (optimization of the excitation and detection efficiency), by reducing the background (as is done in TXRF) or by counting a longer period of time. The value of the attainable detection limits thus depends very much upon the sample, the element considered and the experimental conditions. In wavelength dispersive instruments, values range from 0.1 ppm to 10 ppm are
obtained for medium Z elements (such as Fe) upto 1-5 % for the lightest elements (B, Be). Detection limits for unpolarized ED-XRF are typically a factor 5 to 10 worse, except for TXRF that has absolute detection limits in the pg range. Using synchrotron sources, the detection limits of XRF are generally several order of magnitude better than in case conventional X-ray sources are employed.

3.7.3 Quantitative reliability

The great flexibility, sensitivity and range of the various types of X-ray fluorescence spectrometer make them ideal for quantitative analysis. In common with all analytical methods, quantitative X-ray fluorescence analysis is subject to a number of random and systematic errors that contribute to the final accuracy of the analytical result. Like all instrumental methods of analysis, the potential high precision of X-ray spectrometry can only be translated into high accuracy if the various systematic errors in the analysis process are taken care of. The precision of a wavelength-dispersive system for the measurement of a single, well separated line is typically of the order of 0.1%, and about 0.25% for the energy-dispersive system. A good rule-of-thumb which can be used in X-ray fluorescence analysis to estimate the expected standard deviation $\sigma$ at an analyte concentration level $c$ is given by:

$$\sigma = K (c + 0.1)^{1/2}$$

where $K$ varies between 0.005 and 0.05. For example, at a concentration level $c \approx 25\%$, the expected value of $\sigma$ would be between about 0.025% and 0.25%. A $K$ value of 0.005 would be considered very high quality analysis and a value of 0.05 rather poor quality. The value of $K$ actually obtained under routine laboratory conditions depends upon many factors but with reasonably careful measurements a $K$ value of around 0.02 to 0.03 can be obtained.
3.8 Summary

When an element is bombarded by high-energy particles, orbital electrons may be ejected creating inner orbital atomic vacancies. These vacancies may be filled by transition of outer level electrons giving rise to characteristic X-radiation. X-ray fluorescence spectrometry provides the means of the identification of an element by measurement of its characteristic X-ray emission wavelength of energy.

The method allows the quantization of a given element by first measuring the emitted characteristic line intensity and then relating this intensity of element concentration.

While the roots of the method go back to the early part of this century, where electron excitation systems were employed, it is only during the last 30 years or so that the technique has gained major significance as a routine means of elemental analysis. Wavelength-dispersive spectrometers employ diffraction by a single crystal to separate characteristic wavelengths emitted by the sample. Today, nearly all commercially available X-ray spectrometers use the fluorescence excitation method and employ a sealed X-ray tube as the primary excitation source. The first commercial X-ray spectrometer became available in the early 1950s and although these earlier spectrometers operated only with an air path, they were able to provide qualitative and quantitative information on all elements above atomic number 22 (titanium). Later versions allowed use of helium or vacuum paths that extended the lower atomic number cut-off to around atomic number 9 (fluorine). X-ray detectors used include the flow counter, the scintillation counter and the Si(Li) detector.

The X-ray method has good overall performance characteristics. In particular, the speed, accuracy and versatility of X-ray fluorescence are the most important features among the many that have made it the method of choice in over 30 000 laboratories all over the world.
Most wavelength-dispersive spectrometers fall into two broad categories – single channel and multichannel. Single channel spectrometers are typically employed for both routine and non-routine analysis of a wide range of products, including ferrous and nonferrous alloys, oils, slags and sinters, ores and minerals, thin films, and so on. These systems are very flexible but relative to multichannel spectrometers are somewhat slow. The multichannel wavelength-dispersive instruments are used almost exclusively for routine, high-throughout analysis where the great need is for fast accurate analysis, but where flexibility is of no importance. Energy-dispersive spectrometers exist in various forms, some designed for (on-site or laboratory) bulk analysis, others for surface-specific or microscopic analysis.

Interelement (matrix) effects often complicate quantitative analysis by X-ray fluorescence. However, a wide selection of methods is now available for minimizing these effects, allowing excellent accuracy to be obtained in many cases. Detection limits are achievable down to the low parts per million (ppm) range and it is possible to obtain reasonable responses from as little as a few milligrams of material.
References


Chapter 3. X-ray fluorescence Analysis

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3.4 Matrix effects
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3.5 Data treatment
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3.7 Summary

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