Chapter 4

X-ray based methods of analysis

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4.1 INTRODUCTION

X-rays were discovered by Röntgen in 1878 and were first considered to be a mysterious type of radiation with properties very different from electromagnetic radiation in the ultraviolet, visual and infrared range of the spectrum: Röntgen's first experiments suggested that X-rays could not be reflected, refracted or polarized but instead penetrated fairly deeply into materials, apparently without causing harm or other (permanent) changes. Although it is now well documented that X-rays exhibit analogous characteristics to the radiation of longer wavelengths and that high doses of this type of radiation on (biological) tissues can effectively induce discolourations and other damages, irradiation of inorganic materials with X-rays is generally considered not to cause them any harm. Thus, next to being used for radiographic purposes (see Chapter 2), X-rays are also frequently employed for compositional and structural analysis of cultural heritage (and many other) materials.

A well-established method of quantitative element analysis is X-ray fluorescence (XRF) analysis, which is based on the ionization of the atoms of the material being investigated by an energetic beam of primary X-rays. The characteristic radiation that is emitted by the ionized atoms upon relaxation contains information on the nature and the abundance of the elemental constituents present.

Since XRF meets a number of the requirements of the “ideal method” for non-destructive analysis of cultural heritage materials (see Chapter 1) [1], analysis of objects of artistic and/or archaeological value with conventional XRF is fairly common; it is in fact one of the most often applied methods for obtaining qualitative and semi-quantitative information on the materials these objects are made of [2]. Several textbooks cover the fundamental and methodological aspects of the method and its many variants [3]. In the
specific context of non-destructive analysis of (often) irregular and/or heterogeneous materials, the use of conventional XRF for reliable quantitative analysis is severely hampered by the fact that the irradiated area usually is large. This prevents the separate analysis of details of decorations, distinct features, etc. Also, the irradiation geometry and sample surface are usually non-ideal and/or not well defined, possibly introducing systematic errors in the quantification. Using smaller X-ray beams can circumvent some of these limitations. In such a case, motorized sample movement allows to extend the local analysis capability towards two-dimensional imaging of certain elements on the surface of artefacts. Since many objects of artistic and/or archaeological nature are fairly large and bulky (e.g., statues, oil paintings, vases, treasury objects), recently available instrumentation that can accommodate objects of various shapes and is able to operate in air atmosphere is very useful.

X-ray diffraction (XRD) makes use of the coherent scattering of X-rays by atomic electron clouds and the constructive interference that takes place between rays scattered by regularly spaced series of atoms. The orientation and relative intensity of the reflexes contain information on the crystallographic structure of the materials being studied. Via the use of appropriate data bases, XRD allows to qualitatively identify the compounds present and quantitatively determine their relative abundance in case a mixture of the latter is under scrutiny. It is beyond the scope of this chapter to provide a detailed description on the fundamentals of XRD; more detailed information may be found in many excellent reference texts [4–8].

With the advent of more powerful X-ray sources called synchrotrons, other forms of X-ray spectroscopy, requiring highly monochromatic primary radiation of which the energy or wavelength may be continuously varied, have also come into use. Notably some of the forms of X-ray absorption spectroscopy (XAS) are proving themselves to be useful for non-destructive characterization of cultural heritage materials while these sources have also significantly stimulated the development of the microscopic equivalents of XRF and XRD. By means of XAS it is possible to obtain information on the chemical state of specific (inorganic) constituents of a material, such as the oxidation state of Mn and Fe in weathered glass (often responsible for giving this material its greenish/brownish colour).

In what follows, the fundamentals of the interaction of X-rays with matter are described, after which an overview of the available instrumentation for XRF, XRD and XAS is presented. The chapter concludes with a literature survey on applications of X-ray methods in the cultural heritage sector.
4.2 BASIC PRINCIPLES

4.2.1 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:

\[
\lambda (\text{Å}) = \frac{12.4}{E (\text{keV})} \tag{4.1}
\]

where 1 eV is the kinetic energy of an electron that has been accelerated over a voltage difference of 1 V (1 eV = \( 1.602 \times 10^{-19} \) 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 (10–0.2 Å) range. The established unit of measure for wavelengths in the X-ray region is the angstrom; 1 Å is equal to \( 10^{-10} \) m.

4.2.2 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. 4.1. 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:

\[
I = I_0 e^{-\mu d} \tag{4.2}
\]
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 $E$.

Fig. 4.2 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.

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:

$$\mu(M) = \sum_{i=1}^{n} w_i \mu_i$$ (4.3)

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. 4.1, the absorption of radiation in matter is the cumulative effect of several types of photon–matter interaction processes.

Fig. 4.2. Energy dependence of the mass absorption coefficient $\mu$ of several elements.
that take place in parallel. Accordingly, in the X-ray range the mass attenuation coefficient $\mu_i$ of element $i$ can be expressed as:

$$\mu_i = \tau_i + \sigma_i$$

(4.4)

where $\tau_i$ is the cross-section for photoelectric ionization and $\sigma_i$ the cross-section for scattering interactions. All the above-mentioned cross-sections are energy (or wavelength) dependent. Except at absorption edges (see below), $\mu_i$ is more or less proportional to $Z^4\lambda^3$—see also Chapter 5.

### 4.2.3 The photoelectric effect; X-ray fluorescence

In the photoelectric absorption process (see Fig. 4.3), a photon is completely absorbed by the atom and an (inner shell) electron is ejected. Part of the photon is used to overcome the binding energy $\phi$ of the electron and the rest is transferred to the electron 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 XRF. 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 ionization ($\omega_K < 0.2$) while the medium to heavy elements are preferentially relaxing in a radiative manner ($0.2 < \omega_K < 1.0$). See Fig. 6.3 for a plot on the dependence of $\omega_K$, $\omega_{L3}$ and $\omega_{M5}$ on the atomic number $Z$.

Photoelectric 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 an Fe atom. However, a 5 keV photon can only eject L-shell electrons from such an atom.

Since photoelectric absorption can occur at each of the (excitable) energy levels of the atom, the total photoelectric cross-section $\tau_i$ is the sum of (sub)shell-specific contributions:

$$\tau_i = \tau_{i,K} + \tau_{i,L} + \tau_{i,M} + \cdots$$

$$= \tau_{i,K} + (\tau_{i,L1} + \tau_{i,L2} + \tau_{i,L3}) + (\tau_{i,M1} + \cdots + \tau_{i,M5}) + \cdots$$

(4.5)

In Fig. 4.4, 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

Fig. 4.3. Photoelectric ionization can be followed by either radiative relaxation, causing the emission of characteristic fluorescent X-rays or non-radiative relaxation, involving the emission of Auger electrons.
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 photoelectric 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 XRF 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.

4.2.3.1 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 Kα1-line (non-systematic or Siegbahn nomenclature); similarly, fluorescent X-rays resulting from L3-M5 transitions are better known as Lα1-photons. Table 4.1 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.
Moseley's law is written as:

\[ \frac{1}{\lambda} = K(Z - s)^2 \]  

(4.6)

where \( Z \) is the 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 \( K_{\alpha} \)-lines, the \( L_\alpha \)-lines—see Table 4.1). 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.

Application of the selection rules indicates that in, e.g., the \( K \) series, only \( L_2 \to K \) and \( L_3 \to K \) transitions are allowed. There are equivalent pairs of transitions for the \( L, M, N \), etc., shells. Figure 4.6 shows the lines that are observed in the \( K \) series.

(see Fig. 4.5).
4.2.4 Scattering and diffraction

Scattering is the interaction between radiation and matter which causes a 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 XRD. 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:

$$\sigma_i = \sigma_{R,i} + \sigma_{C,i}$$

(4.7)

Fig. 4.5. Variation of characteristic line wavelengths with atomic number.

Fig. 4.6. Characteristic X-ray lines observed in the K series.
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. 4.7), with initial energy $E$, will have a lower energy $E'$ given by the
Compton equation:

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

where $m_0$ denotes the electron rest mass.

4.2.4.1 Interference and diffraction

When a wave front of X-rays strikes an atom, the electrons in this atom will
scatter the X-rays (see above: Rayleigh scattering). The elastically scattered
wave is immediately re-emitted in all directions and can be imagined as a
spherical wave front (see Fig. 4.8).

When a line of identical atoms, a distance $a$ apart, is considered, and a
wave (with wavelength $\lambda$ and wave vector $\vec{k}$, where $|\vec{k}| = 1/\lambda$) approaches this
line under an angle $\theta$, the wave front arriving at the second atom will have a
path different $\delta_1 = OP = a \cos(\theta)$ relative to that arriving at the first atom.
(see Fig. 4.9). When two rays, scattered under an angle $\varphi$ relative to the row of atoms are considered, a second path difference $\delta_2 = QR = a \cos(\varphi)$ is observed that will partially compensate this offset, so that finally, the path difference between the two rays scattered at both atoms is given by:

$$D = d_1 + d_2 = (QR - OP) = a[\cos(\theta) - \cos(\varphi)]$$

Only when this path difference is equal to an integral multiple $n$ of the wavelength $\lambda$, constructive interference will take place between the scattered rays, giving rise to an increased intensity in all directions $\varphi$ relative to the line of atoms. Depending on the value of the order $n_1$ ($n_1 = 0, 1, 2, \ldots$), this set of directions form cones of decreasing opening angle, as shown in Fig. 4.10 for the cases of $\theta = 90^\circ$ and $\theta \neq 90^\circ$. The condition $\Delta = n_1\lambda$ can also be expressed by making use of the scalar product between the wave vectors of the incident ($\vec{k}_0$) and scattered waves ($\vec{k}_1$) and the vector $\vec{a}$ between

Fig. 4.8. Incident plane wave and scattered spherical wave during XRD experiments.
Fig. 4.9. Path difference between rays scattered at two adjacent atoms spaced a distance $a$ apart.

Fig. 4.10. Diffraction cones (left) produced by interaction of a planar X-ray wave front with a linear array of atoms for (a) $\theta = 90^\circ$ and (b) $\theta \neq 90^\circ$. 
adjacent atoms along the line:

\[ \mathbf{a} \cdot \mathbf{k}_0 - \mathbf{a} \cdot \mathbf{k}_1 = n_1 \]  \hspace{1cm} (4.9)

When along some angle relative to the first, a second line of regularly spaced atoms is considered, characterized by a spacing vector \( \mathbf{b} \) (thus forming a two-dimensional net), this second line will independently generate a series of cones at the same origin, but centred around \( \mathbf{b} \). The intersection of both sets of cones will be a series of lines (see Fig. 4.11) and only along directions pointing to these lines, strong constructive interference will be observed.

In case of irradiation of a three-dimensional lattice (characterized by a unit cell with vectors \( \mathbf{a}, \mathbf{b}, \mathbf{c} \)), the incident X-ray beam \( \mathbf{k}_0 \) will be diffracted along those directions \( \mathbf{k}_1 \) that simultaneously fulfil the following equations, termed the Laue conditions:

\[
\begin{align*}
\mathbf{a} \cdot (\mathbf{k}_0 - \mathbf{k}_1) &= n_1 \\
\mathbf{b} \cdot (\mathbf{k}_0 - \mathbf{k}_1) &= n_2 \\
\mathbf{c} \cdot (\mathbf{k}_0 - \mathbf{k}_1) &= n_3
\end{align*}
\]  \hspace{1cm} (4.10)

Fig. 4.11. Diffraction induced by a two-dimensional net of atoms is only strong along intersecting lines between two cones.
corresponding to the intersection of three sets of cones centered around \( \vec{a}, \vec{b} \) and \( \vec{c} \).

The result is that, for a three-dimensional lattice of atoms irradiated by X-radiation, strong constructive interference will only occur in specific directions and for specific conditions of incidence. In 1913 Bragg realized that the conditions for constructive interference of X-rays are equivalent to that of a simple plane reflecting the X-rays like an optical mirror. This is shown in Fig. 4.12 where the incident radiation strikes the planes of atoms at an angle \( \theta \). For constructive interference, the path difference \( GY + YH \) between rays A and B (reflected, respectively, off the first and second plane, separated a distance \( d \) from each other) must be an integral multiple of the wavelength \( \lambda \). Since \( GY = YH = d \sin(\theta) \), it follows that:

\[
2d \sin \theta = n\lambda
\]

(4.11)

This equation is known as Bragg’s law and is very important in XRD and crystallography.

When \( \theta \) is maximum, i.e., at 90°, the diffracted rays are back-reflected by the crystal and \( \sin \theta = 1 \) so that \( 2d = n\lambda \); thus the smallest \( d \)-spacing than can be observed with X-rays in any crystal will be equal to one-half of the wavelength of the incident radiation.

From Bragg’s law it follows that when a crystal is irradiated with a beam of X-rays of known wavelength \( \lambda \) and this beam is diffracted over an angle \( 2\theta \),

Fig. 4.12. Geometry for Bragg reflection of an X-ray wave front by sets of crystallographic planes spaced a distance \( d \) apart.
it is possible to determine the interplanar spacing \( d \) of the set of atomic planes inside the crystal that caused the diffraction. By either varying the wavelength or the orientation of the impinging beam on the crystal, many principal planes of a crystal can be brought into diffracting mode. The set of recorded \( d \)-spacings can then be employed to identify the crystallographic phase that was irradiated and/or to determine the dimensions of the unit cell.

### 4.2.5 X-ray absorption fine structure and spectroscopy

As shown in Fig. 4.2, the mass absorption coefficient vs. energy curves of the elements feature sharp discontinuities, called absorption edges, corresponding to the energies required for electronic transitions from deep core levels to the vacuum level. However, when one considers in more detail the shape of the \( \mu(E) \) vs. \( E \) curves in the immediate vicinity of these edges, additional features become apparent. XAS is a method that employs this fine structure to extract information on the chemical environment of the absorbing atom.

In an X-ray absorption experiment, a monochromatic X-ray beam is directed at the sample. The photon energy of the X-rays is gradually increased such that it traverses one of the absorption edges of the elements contained within the sample. Below the absorption edge, the photons cannot excite the electrons of the relevant atomic level and thus absorption is low. Transitions at energies \( E \) smaller than the binding energy \( E_0 \) occur only when the absorbing atoms possesses localized unoccupied (or only partially occupied) states, e.g., d-orbitals in the case of transition metals (see Fig. 4.13a). When the photon energy is just sufficient to excite the electrons \((E = E_0)\), then a large increase in absorption occurs known as the absorption edge. At X-ray energies higher than \( E_0 \), transitions to continuum states take place, i.e., to electronic states not localized on the absorbing atom. The resulting photoelectrons have a low kinetic energy and can be backscattered by the electron shells of the atoms surrounding the emitting atom (see Fig. 4.13c–e). The photoelectrons (with kinetic energy \( E - E_0 \)) leaving the atoms can also be regarded as an expanding spherical wave with wavenumber \( k \) given by:

\[
k = \sqrt{\frac{2m_0}{\hbar^2}(E - E_0)}
\]

An X-ray absorption spectrum is typically divided into two energy regions: the X-ray absorption near-edge structure or XANES region, which extends
from a few eV below an element’s absorption edge to about 50 eV above the edge, and the extended X-ray absorption fine structure or EXAFS region, which extends from about 50 eV to as much as 1000 eV above the edge (Fig. 4.13). The XANES region is also sometimes referred to as the near-edge X-ray absorption fine structure or NEXAFS region. The range just before the edge is called the pre-edge region (see Fig. 4.13a). The physics of the processes responsible for XANES and EXAFS spectral features is different; thus, these spectral regions provide different types of information about an element and its local environment.

XANES can provide information about vacant orbitals, the electronic configuration and site symmetry of the absorbing atom. The absolute position of the edge contains information on the oxidation state of the absorbing atom. In general, with increasing oxidation state of the central atom [e.g., Mn$^0$, Mn$^{+2}$, Mn$^{+3}$, ..., Mn$^{+7}$], the absorption profiles shift towards higher energies by a few eV per oxidation state. In the near-edge region, multiple scattering events dominate (see Fig. 4.13b). Theoretical multiple

Fig. 4.13. Cr-K edge X-ray absorption spectrum of K$_2$CrO$_4$; the physical processes leading to the different features of an X-ray absorption spectrum are indicated, as well as the XANES and EXAFS regions. (a) Pre-edge peak(s) caused by transitions to unoccupied orbitals; (b) multiple scattering peaks; (c) single scattering region showing oscillations on the absorption curve caused by (d) destructive interferences and (e) constructive interference between the outgoing and back-reflected photo-electron waves.
scattering calculations can be compared with experimental XANES spectra in order to determine the geometrical arrangement of the atoms surrounding the absorbing atom. Hence the technique provides complementary information to EXAFS.

The basis of physical process leading to the oscillations of the absorption in the EXAFS region is the interference between the photoelectron wave leaving the emitting atom with its backscattered equivalents, as pictorially represented in Fig. 4.13b and c. Depending on the wavelength (i.e., on the energy of the ejected photoelectron) of the interfering waves and the distance between the central atom and the backscattering neighbours, the interference can be constructive, leading to a higher value for the absorption coefficient \( \mu \) (see Fig. 4.13b) or destructive, giving rise to a lower value for \( \mu \) (Fig. 4.13c) relative to the case when the central atom would not have any backscattering neighbours. The net result is a series of oscillations on the high photon energy side of the absorption edge, called the X-ray absorption fine structure (XAFS).

After transforming the energy scale of the XAS spectrum to wave numbers, the EXAFS oscillations \( \chi(k) \) are isolated from the total absorption coefficient curve by fitting a “background absorption” curve \( \mu_0(k) \) to it and using the expression:

\[
\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}
\]

The different coordination shells around the absorbing atom each contribute to the total EXAFS signal. By means of a Fourier transformation, \( k^n \chi(k) \) (where \( n \) is an integer, e.g., 2 or 3) the contributions can be sorted, yielding a radial distribution function (RDF) around the absorbing atom. This function shows peaks at a distance where the neighbouring atoms that cause the EXAFS oscillations are situated. The RDFs contain information on the environment of the absorbing element out to ca. 5 Å. By isolating and individually fitting the contributions to \( \chi(k) \), the true interatomic distances and number of neighbouring atoms per shell can be determined.

More detailed information on the theory, techniques, and applications of XAS can be found in the book by Koningsberger and Prins [9]. Stern [10] and Durham [11] describe in a relatively brief form the theory of EXAFS and XANES spectroscopies. Applications of XAS in materials and earth sciences are summarized by Wong [12] and Brown et al. [13].

Since its development in the early 1970s, synchrotron-based XAS has proven itself to be a versatile structural probe for studying the local environments of cations in a variety of materials ranging from crystalline...
solids, glasses, and high-temperature liquids to aqueous sorption systems which involve metal complexes associated with (or sorbed at) solid/water interfaces. XAS is an atom-specific, local structure probe. Both physical and electronic structure are probed, but the probe range is generally only the first two shells of atoms around the absorber atom, which is generally less than 5–6 Å. In some special cases (e.g., when the sample is highly crystalline and the second and more distant shells around the absorbing atom contain atoms that backscatter photoelectrons well), information about more distant shells can be obtained, usually with greater uncertainty than in the near-shell cases.

XAS generally requires a synchrotron X-ray source for several important reasons:

– A high X-ray flux is required in an XAS experiment in order to obtain high signal-to-noise data in a reasonable time frame (of the order of 30–40 min per spectrum). This requirement is particularly critical if the element of interest is at low concentration in a sample. Synchrotron sources provide X-rays of five or more orders of magnitude greater flux than conventional laboratory X-ray sources.

– A broad spectral range at uniformly high flux is required because a typical X-ray absorption spectrum covers about 1000 eV. Tunable monochromators with appropriate d-spacings can be used to scan through a broad range of energy; thus one can choose the most appropriate energy range for an experiment.

– High stability in flux, energy, and beam position is required in an XAS experiment and can be achieved with a synchrotron X-ray source.

The main advantages of XAS over those of other structural methods are its element specificity and the fact that it can be used with practically any atom in any state of organization (solid, liquid, or gas). In addition, the sensitivity of XAS can be at the tens to hundreds of ppm level of an element, so that it can be used to study the structural environment of an element at trace levels in a chemically complex matrix. These attributes coupled with its ability to provide quantitative information on interatomic distances and the number and identities of atoms in the first and, in favourable cases, the second shell around an absorber, make XAS an extremely versatile and often unique probe of an atom’s local environment. The local nature of the XAS probe is both an advantage (e.g., XAS is particularly useful in studying the environment of atoms in amorphous materials where there is no long-range order and where X-ray scattering methods suffer from lack of element specificity) and a disadvantage (e.g., XAS provides essentially no information...
on long-range order in a solid, including cation order–disorder among non-
equivalent sites in a crystal structure). Disadvantages of XAS relative to
XRD includes a limited resolution for sets of similar bond lengths and a high
sensitivity to disorder.

4.3 INSTRUMENTATION FOR X-RAY INVESTIGATIONS

XRF 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 analysed.
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.

WDXRF 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 EDXRF 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 microscopic XRF (μ-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.

In XRD instruments, on the other hand, a (quasi)monochromatic beam is
normally employed to irradiate the samples, unless a form of energy-
dispersive diffraction is being employed. In instruments employing
laboratory sources, the wavelength of the radiation is fixed and equal to
the most intense emission line of the X-ray tube anode being used. A typical
X-ray tube is schematically shown in Fig. 4.14. Frequently encountered
anode materials and the corresponding primary wavelengths and X-ray tube
operating conditions are listed in Table 4.2.

XAS makes use of synchrotron radiation sources and double crystal
(or more sophisticated) monochromators in order to reach a level of
monochromaticity ($\Delta E/E$ or $\Delta \lambda/\lambda$) of around $10^{-4}$ (see below) in experimental setups dedicated to this type of measurements.

### 4.3.1 X-ray sources

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.

<table>
<thead>
<tr>
<th>Anode material</th>
<th>Cr</th>
<th>Fe</th>
<th>Cu</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>24</td>
<td>26</td>
<td>29</td>
<td>42</td>
</tr>
<tr>
<td>$\lambda(K_{\alpha 1})$ (Å)</td>
<td>2.2896</td>
<td>1.9360</td>
<td>1.5405</td>
<td>0.70926</td>
</tr>
<tr>
<td>$\lambda(K_{\alpha 2})$ (Å)</td>
<td>2.2935</td>
<td>1.9399</td>
<td>1.5443</td>
<td>0.71354</td>
</tr>
<tr>
<td>$\lambda(K_{\beta})$ (Å)</td>
<td>2.2909</td>
<td>1.9373</td>
<td>1.5418</td>
<td>0.71069</td>
</tr>
<tr>
<td>$\lambda(K_{\beta 1})$ (Å)</td>
<td>2.0848</td>
<td>1.7565</td>
<td>1.3922</td>
<td>0.63225</td>
</tr>
<tr>
<td>Critical potential (kV)</td>
<td>5.99</td>
<td>7.11</td>
<td>8.98</td>
<td>20.0</td>
</tr>
<tr>
<td>Operating voltage range (kV)</td>
<td>30–40</td>
<td>35–45</td>
<td>35–45</td>
<td>50–55</td>
</tr>
<tr>
<td>Operating current (mA)</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>
(In addition, characteristic X-ray lines (see below) of the target materials are also 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 $\lambda_{\text{min}}$ (Å) = $12.4/E_{\text{max}}$ (keV) = $12.4/V$ (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. 4.15 bremsstrahlung spectra emitted by X-ray tubes operated at different accelerating potentials are shown.

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 are 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. Figure 4.14 shows a schematic cross-section of a sealed X-ray tube. 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, the bremsstrahlung continuum is produced upon which the characteristic lines of the anode material are superimposed (see Fig. 4.15). The shape of the emission spectrum can be modified by changing the electron acceleration voltage. 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.

In typical X-ray tubes employed in XRF spectrometers, accelerating voltages of 25–50 kV are used, while electron currents in the range of 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 anode of high-power tubes (>100 W) usually is water-cooled to avoid 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/mm$^2$) 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 percent 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.

In most XRD experiments only one well-defined wavelength of radiation is needed. Quasi-monochromatic X-rays of fixed wavelength can be obtained by filtering the white spectrum emerging from an X-ray tube. Filtering is probably the cheapest and simplest way of obtaining approximately monochromatic X-rays. One can achieve far “cleaner” radiation by using a monochromator, however, the cost of a monochromator could be 10,000 times the cost of a thin sliver of metal of the correct thickness. Table 4.3 lists suitable filters for various X-ray generators. In Fig. 4.16, next to an X-ray
emission curve of a Mo-anode X-ray tube, the absorption curve of a Zr foil is also shown. The absorption edge of Zr falls just in between the K\(_{\alpha}\) and K\(_{\beta}\) lines of Mo. In other words, if we pass Mo radiation through a sheet of Zr metal, the Zr metal will absorb the Mo-K\(_{\beta}\) radiation far more strongly than the K\(_{\alpha}\) photons. Figure 4.16 also shows schematically what the resulting distribution of radiation intensities will look like after filtering.

Radioactive \(\alpha\)-, \(\beta\)-, and \(\gamma\)-sources may also be employed for EDXRF 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 \(^{244}\)Cm, with a half-life (\(t_{1/2}\)) of 17.8 y that emits 5.76 and 5.81 MeV \(\alpha\)-particles, and \(^{210}\)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 bremsstrahlung radiation in a target to be used for subsequent sample excitation. \(^{22}\)Na (\(t_{1/2} = 2.6\) y), \(^{85}\)Kr (\(t_{1/2} = 10.7\) y) and \(^{63}\)Ni (\(t_{1/2} = 100\) y) are \(\beta\)-emitters that can be used for the former purpose, emitting, respectively, \(\beta^-\)-particles of ca. 550, 670 and 66 keV. For bremsstrahlung production, \(^{147}\)Pm (\(t_{1/2} = 2.6\) y, 225 keV) in combination with a Zr target and \(^{3}\)H (\(t_{1/2} = 12.4\) y, 19 keV, Ti target) are useful.

In Table 4.4, some characteristics of radioactive 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,
an 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, an Mn K–L $\alpha$ (Mn-K$_\alpha$) or K–M $\alpha$ (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.

In **Fig. 4.17**, the range of elements that can be usefully analysed by means of various radioactive and X-ray tubes sources is summarized. In a number of specialized cases, X-ray analysis 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

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**Fig. 4.16.** Original and filtered emission curves of a Mo-anode X-ray tube. The absorption curve of Zr is also indicated.
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 when the emission of radiation is induced by bending magnets (see Fig. 4.18a), and the most simple way of employing SR is to use the full white beam to irradiate the sample (see below—\(\mu\)-XRF). When more sophisticated magnetic arrays called undulators are used to produce the radiation, much more intense X-ray beams can be generated. The photons are emitted in specific energy bands called harmonics (see Fig. 4.18b). Undulators are complex multi-pole magnetic structures of which a number of parameters such as the distance between the magnet poles and the magnetic field strength can be modified during experiments to suit the users needs.

Figure 4.18b shows the energy spectrum of the undulator device at ESRF ID22. By changing undulator parameters such as the gap width and the magnetic field strength, the energy of the harmonics can be adjusted so that the output flux of an undulator in a specific energy-range can be optimized. In view of their quasi-monochromatic nature, undulator sources therefore are more suitable for performing \(\mu\)-XRF experiments involving monochromatic primary micro-beams, of which the energy can optionally be tuned. In this manner, 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 synchrotron radiation, 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.

<table>
<thead>
<tr>
<th>Radioisotope</th>
<th>Half-life (years)</th>
<th>X-ray or (\gamma)-ray energy (keV)</th>
<th>Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{55}\text{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}\text{Cm})</td>
<td>88</td>
<td>14.6–22 (U-L X-rays)</td>
<td></td>
</tr>
<tr>
<td>(^{109}\text{Cd})</td>
<td>1.3</td>
<td>22–25 (Ag-K X-rays)</td>
<td>(8 \times 10^6)</td>
</tr>
<tr>
<td>(^{125}\text{I})</td>
<td>0.16</td>
<td>27–32 (Te-K X-rays)</td>
<td></td>
</tr>
<tr>
<td>(^{241}\text{Am})</td>
<td>433</td>
<td>59.6 ((\gamma)-ray)</td>
<td>(6 \times 10^7)</td>
</tr>
<tr>
<td>(^{153}\text{Gd})</td>
<td>0.66</td>
<td>41.48 (Eu-K X-rays)</td>
<td>(4 \times 10^8)</td>
</tr>
<tr>
<td>(^{57}\text{Co})</td>
<td>0.74</td>
<td>122.136 ((\gamma)-ray)</td>
<td>(4 \times 10^6)</td>
</tr>
</tbody>
</table>
The combination of a high primary beam intensity and low spectral background causes detection limit values of synchrotron XRF to go down to the ppb level. A disadvantage of the use of synchrotron radiation 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.

The fact that synchrotron radiation can be efficiently focused into (sub)microscopic beams also permits very small samples to be employed during XAS and XRD experiments.

Fig. 4.17. Range of elements that can be analysed using (top) radioactive sources, (bottom) X-ray tubes with different anodes, showing excitation of K- and L-lines.
4.3.2 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 the interaction between an 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 is 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\(_a\) 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 origins (e.g., the As-K\(_{\alpha1}\) line at 10.543 keV and the Pb-L\(_{\alpha1}\) line at 10.549 keV).

In WDXRF spectrometers (see section 4.3.3.1), gas flow proportional counters (for long wavelengths, \(\lambda > 2\ \text{Å}\)) and scintillation counters (for wavelengths shorter than 2 Å) 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 a sufficient resolution to separate multiple wavelengths/energies on its own, they are employed together with an analysing crystal. In case of energy-dispersive spectrometry, solid-state detectors of higher resolution are used.

A gas flow proportional counter (see Fig. 4.19) 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 an inert gas and a 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 $\varepsilon$ 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:

$$n = \frac{E}{\varepsilon}$$

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

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Fig. 4.19. Schematics of a gas-filled proportional counter.
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 1.5 Å. For this shorter wavelength region it is common to use a scintillation counter (see Fig. 4.20). 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 higher 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 the 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 200–300 ns after the arrival of each photon; this implies that count rates of up to $10^6$ photons/s 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.
X-ray based methods of analysis

Fig. 4.20. Schematics of a scintillator detector.
Because of their operation principles, these detectors have an inherent simultaneous multi-element 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$_2$) 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 typically is a disk of very pure Si or Ge with dimensions of 4–10 mm diameter and 3–5 mm thickness. Even after careful production of the Si ingots from which the disks are cut, some trace impurities in the Si lattice will be left. 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$_2$ by placing it in a vacuum cryostat. At $-196^\circ$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.

Figure 4.21 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 amplifiers 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 multi-channel analyser (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-K\(_{\alpha1}\) photon \((E = 8.05\) 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. 4.22.

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. This gives rise to the bell-shaped X-ray peaks in the spectrum. This line-broadening is caused by statistical fluctuations in the number of electron–hole pairs created when an X-ray photon of a given energy enters the detector; electronic noise in the amplifiers causes 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

Fig. 4.21. Scheme of the working principle of a Si(Li) detector.
Fig. 4.22. Energy-dispersive XRF spectrum of a multi-element standard, obtained in a TXRF spectrometer.
conventionally is expressed as the full-width-at-half-maximum of the Mn-Kα (Mn K–L₂,3) 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 10–30 μs; conventional EDXRF spectrometers can therefore only operate at count rates up to 40,000 cps. 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.

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 in to be much smaller. These type of detectors is suitable for employment in portable equipment.

Thermoelectrically cooled Si-PIN, Cd₁₋ₓZnₓTe (CZT) and HgI₂ detectors are fairly inexpensive devices. The currently available Si-PIN diode detectors mostly have a thickness of about 300 μm 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-Kα, i.e., slightly worse than that of Si(Li) or HPGe detectors. CZT detectors are targeted towards the higher energy range with a thickness of up to 2 mm, allow efficient detection of X-rays up to 150 keV with a resolution of ca. 250 eV at Mn-Kα (5.9 keV) and 1 keV at 60 keV. Similarly, HgI₂ detectors (with thicknesses of a few millimetres) can also be used in this range with a resolution of ca. 200 eV at Mn-Kα.

A very useful and more recent 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 cm² diameter. They still show excellent spectroscopic behaviour at count rates as high as 2 × 10^6 counts/cm²/s. The compact design, the relatively low price, the absence of the need for liquid nitrogen cooling, the high count rate capability and the insensitivity 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. 4.23. It is clear that scintillators and proportional counters are not even able to separate the Kα-lines of adjacent elements whereas this is the case for most of
the solid-state detectors. A more extensive overview of recently developed X-ray detectors can be found elsewhere [14].

In XRD instruments, typically employing radiation in the 8–18 keV range, usually collimated scintillator detectors are mounted on the 2θ arm of the goniometer.

In XAS setups, in many cases, ionization chambers similar to the above-mentioned proportional counters are employed to measure the incoming and transmitted X-ray beam intensities.

4.3.3 X-ray fluorescence instrumentation

4.3.3.1 Wavelength-dispersive XRF

A typical WDXRF system consists of an X-ray tube, a specimen support holder, a primary collimator, an analysing crystal and a tandem detector. The typical WDXRF irradiation/detection geometry is shown in Fig. 4.24. 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 characteristic wavelengths that is coming from the sample, such that each wavelength $\lambda$ will diffract at a specific angle $\theta$, given by Braggs law.
A goniometer is used to maintain the required $\theta/2\theta$ relationship between sample and crystal/detector.

Prior to impinging on the analyser 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 $73^\circ$, the maximum wavelength that can be diffracted by a crystal of spacing $d$ is equal to ca. $1.9d$.

The angular dispersion $d\theta/d\lambda$ of a crystal with spacing $2d$ is given by:

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

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, 4–6 different analyser 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 \( \theta \) spectrum, but the angular dispersion of the analysing crystal itself and the intrinsic width of the diffraction lines also play a role.

In Table 4.5, some characteristics of a few commonly employed analyser crystals are listed. Classically, large single crystals have been used as dispersive elements. For dispersion of long wavelengths (>8 Å), only a limited number of natural materials are available; the most commonly employed is thallium acid phthalate (TAP, \( 2d = 26.3 \) Å), 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 1980s 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 4–6 improvement in peak intensities compared to TAP crystals can be achieved.

Among wavelength-dispersive spectrometers, a distinction can be made between single-channel instruments and multi-channel spectrometers. In the former type of instrument, a single-dispersive crystal/detector combination is used to sequentially measure the X-ray intensity emitted by a sample at a series of wavelengths when this sample is irradiated with a 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 analyser crystal is continuously varied; in order to maintain an identical angle between analyser crystal and detector, the

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Planes</th>
<th>( 2d ) (Å)</th>
<th>K-line range</th>
<th>L-line range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium fluoride (LiF)</td>
<td>220</td>
<td>2.848</td>
<td>&gt;Ti</td>
<td>&gt;La</td>
</tr>
<tr>
<td>Lithium fluoride (LiF)</td>
<td>200</td>
<td>4.028</td>
<td>&gt;K</td>
<td>&gt;Cd</td>
</tr>
<tr>
<td>Pentaerythritol (PET)</td>
<td>002</td>
<td>8.742</td>
<td>Al–K</td>
<td>–</td>
</tr>
<tr>
<td>Thallium acid phthalate (TAP)</td>
<td>001</td>
<td>26.4</td>
<td>F–Na</td>
<td>–</td>
</tr>
<tr>
<td>LSMs</td>
<td>–</td>
<td>50–120</td>
<td>Be–F</td>
<td>–</td>
</tr>
</tbody>
</table>

TABLE 4.5
Analysing crystals used in wavelength-dispersive X-ray spectrometry
latter moves at double the angular speed as the crystal. In this manner, X-ray intensity vs. 2θ diagrams are obtained. By means of tables, the recorded peaks can be assigned to the characteristic lines of one or more elements. In Fig. 4.25, a typical 2θ-spectrum obtained from a brass sample is shown.

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 a 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 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 multi-sample handling facilities and automated. Both are capable of precision of the order of a few tenths of a percent and both have sensitivities down to the ppm level. Single-channel wavelength-dispersive spectrometers are typically employed for both routine and non-routine analysis of a wide range of products, including ferrous and non-ferrous alloys, oils, slags and sinters, ores and minerals and thin films. These systems are very flexible but, relative to multi-channel spectrometers, are somewhat slow. The multi-channel 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.

### 4.3.3.2 Energy-dispersive XRF for bulk analysis

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 an 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
Fig. 4.25. Wavelength-dispersive X-ray spectrum of a brass sample, showing the characteristic lines of the major elements Cu and Zn, and the minor constituents Cr, Fe, Ni and Pb, superimposed on a continuous background.
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 detection limits that can be attained by the instrument strongly depend on the sophistication with which this is done.

In Fig. 4.26a, the most simple of EDXRF instrumental configuration 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 beams 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.

Fig. 4.26. Schematic drawings of (a) a direct-excitation XRF instrument, (b) a secondary target XRF instrument, (c) a polarized XRF instrument employing a cartesian (XYZ) irradiation geometry.
The schematic of a “secondary target” EDXRF system is shown in Fig. 4.26b. 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\textsubscript{\textalpha} and Mo-K\textsubscript{\textbeta}). 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\textsubscript{\textbeta} component of the secondary target radiation (e.g., a Zr foil in case of a Mo target; see Fig. 4.16), 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, an Rh secondary target may be selected while for optimal detection of Cr in the same material, a Cu target would be more beneficial.

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.

Figure 4.26c 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. 4.26c. For polarization of medium-to-hard radiation (\(E > 10\) 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 \(E < 10\) keV, photoelectric absorption dominates over
scattering. In the region 1–10 keV, radiation can be polarized through Bragg
diffraction over $2\theta \approx 90^\circ$ by using a suitable crystal. For example, highly
oriented pyrolytic graphite (HOPG) is an excellent Bragg polarizer for the
(002) reflection of the Rh-L$_{\alpha}$ radiation ($\theta = 43.2^\circ$). Multiple layer scatterers,
for example consisting of a thin layer of HOPG glued on top of an Al$_2$O$_3$
substrate, in combination with an Rh tube are useful to determine a wide
range of elements simultaneously with good detection limits and
sensitivities.

4.3.3.3 Portable EDXRF instruments

Next to EDXRF spectrometers that are intended for use in the laboratory, a
number of portable EDXRF instruments are also commercially available.
These devices are used in various fields for on-site analysis of works of art,
environmental samples, forensic medicine, industrial products, waste
materials, etc. In its simplest form, the instruments consist of one or more
radioisotope sources combined with a scintillation or gas proportional
counter. However, also combinations of radiosources with thermoelectronically
cooled solid-state detectors are available in compact and light-weight
packages (i.e., below 1 kg). In Fig. 4.27, schematics of various types of
radiosource-based EDXRF spectrometers are shown. The X-ray source can
be 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. Figure 4.27 also shows X-ray sources of
other shapes, requiring a different type of shielding. Next to equipment using
radioisotopes 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.

As shown in Fig. 4.28, handheld devices allowing for rapid on-site
identification of alloys and other inorganic materials are available from

Fig. 4.27. Radioisotope-excited X-ray fluorescence analysis by means of (left) an
annular source, (middle) a central source and (right) a side-looking source.
various companies, such as TN technologies, Oxford Instruments plc., Niton Inc., Metorex International Oy and EDAX Portable Products Division [15]. The most recent versions of these devices incorporate several radioisotope sources (e.g., a combination of $^{55}$Fe, $^{109}$Cd and $^{241}$Am is frequently encountered) in combination with a compact solid-state detector such as a drift chamber detector or a PIN diode. Usually such analysers are equipped with “standardless” data-processing software that is intended for use in a specific type of application, such as the sorting of waste metal or the detection of hazardous waste, by means of which the quantitative results can be calculated and displayed to the user immediately after the data collection. An overview of currently available instruments can be found in Ref. [16].
4.3.3.4 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. The 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 45deg; while the detector is placed normal to the incident beam so that the angle between sample and detector is also 45deg.; The principle setup of TXRF is shown in Fig. 4.29.

The largest angle at which total external reflection still takes place is called the critical angle of total reflection $\phi_{\text{crit}}$. 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 centre 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 beams, the fluorescent signal is practically twice as intense as in the standard EDXRF excitation mode. 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 anode X-ray tube) or 17.5 keV (from a Mo anode tube). With higher energies

Fig. 4.29. Schematic layout of a TXRF spectrometer.
in the exciting spectrum, adjustments must be made for the proper incident angle below the critical angle, which (for glass reflectors) is given by:

\[ \phi_{\text{crit}}(\text{mrad}) = 20.7/E(\text{keV})^{1/2}(\text{g/cm}^3) \] (4.14)

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) Depending on the X-ray source and the spectral modification devices, the absolute limits of detection are in the pg range for instruments employing 2–3 kW X-ray tubes and in the fg range when synchrotron radiation excitation is used (see below).

Figure 4.22 shows a typical TXRF spectrum. TXRF permits to simultaneously determine minor to trace elements in samples of small volume. Additional advantages are insensitivity to matrix effects, easy calibration, fast analysis times and low costs.

4.3.3.5 Microscopic XRF

The basic measuring strategy of microscopic X-ray fluorescence (\(\mu\)-XRF) analysis is illustrated in Fig. 4.30. This micro-analytical 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 for sensitive micro-analysis. Techniques to do this have only recently appeared; in the past, X-rays were considered to be notably difficult to focus into beam of small dimensions. Variants on the basic mode of operation either reside with the method employed for X-ray beam concentration/focussing or with the source
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![Diagram of X-ray optics](image)

**Fig. 4.30. Principle of \(\mu\)-XRF.**

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 \(\mu\)m diameter spots, has made the development of \(\mu\)-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 detection limits of around 10 ppm have been reported for transition elements. At synchrotron facilities, the capabilities of the \(\mu\)-XRF method (both regarding spot sizes and detection limits) are significantly better: fg to ag level absolute detection limits are obtained with beams as small as 0.5–2 \(\mu\)m 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 detection limit values in the 10–100 ppb range in biological materials. The application of \(\mu\)-XRF to a great variety of problems and materials has been described, including geochemistry, archaeology, industrial problems and environmental studies [17]. 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.

**Microfocussing X-ray optics**

**Figure 4.31** illustrates the functioning principle of capillary optics. Through repeated total external reflection on the inner walls of the tube, X-ray photons are transported along the length of the tubes; thus, straight capillaries act as effective apertures over a wide energy range (0–40 keV and beyond). Since metal pin holes or cross-slit systems are not effective to collimate the high-energy portions of the white beam of a
synchrotron source to a micro-spot with well-defined shape, straight capillaries are employed for this purpose. However, these devices do not “concentrate” the X-ray beam. In conical capillaries, the X-ray beam that enters the wide end of the taper is gradually “squeezed” to the taper dimensions at the fine end during the many reflections that take place along the way. In case ellipsoidal lead-glass capillaries are employed \[18\], the capillary is positioned in such a way that its tip is about 0.5–1 mm away from the sample surface. Inside ellipsoidal capillaries, the X-ray photons are subject to only one or a few reflections and part of the radiation is focused in this manner. A polycapillary lens consists of a large number of hollow glass fibres. The fibres are bent towards a common focal point, situated outside the polycapillary. While passing through these tubes, photons are redirected towards the focal point, resulting in focussing of the X-ray beam \[19\]. Polycapillary lenses can operate in the energy range from 2 to 30 keV and have a number of other properties that render them advantageous for use in \(\mu\)-XRF and \(\mu\)-XANES experiments. They have a focal point that is situated outside the lens; the focal distance is typically a few millimetres to a few centimetres, allowing for a safe distance between optic and sample. Also, the compact size of these devices contributes to their practical applicability.

Mono- and polycapillary X-ray optics are very frequently used in \(\mu\)-XRF instruments since they are compact, robust and relatively inexpensive optical elements. In almost all laboratory \(\mu\)-XRF apparatus either capillary optics or pin-hole apertures are employed for focusing or collimating the polychromatic spectrum emerging from a micro-focus X-ray tube.

Fig. 4.31. Functioning principle of capillary optics: (a) total external reflection of an optical flat surface; (b) multiple total reflection on the inner surface of a straight capillary; (c) X-ray photon propagation in a bent capillary (degree of bending is strongly exaggerated); (d) point-to-point focusing of X-rays with a polycapillary lens.
Capillary optics have the additional advantage of being “non-imaging optics”, indicating that the diameter of the X-ray micro-beams they generate is largely independent of the size of the X-ray source employed. Generally, polycapillary optics produce beam sizes in the range 10–50 μm while operating efficiently in the 5–25 keV range. A more detailed treatment of their characteristics can be found elsewhere [20].

At synchrotron μ-XRF setups, also more sophisticated types of optics are also in use: compound refractive lenses (CRL) [21], Fresnel zone plates (FZP) [22] and curved mirror systems are examples of the latter [23]. These imaging optics are capable of producing X-ray beams with submicron dimensions but can only be used at synchrotron sources such as the European Synchrotron Radiation Facility (Grenoble, France).

**Laboratory μ-XRF equipment**

Several commercial companies offer laboratory μ-XRF instruments, including EDAX and Horiba. In Fig. 4.32, photographs of the exterior and interior of the EDAX Eagle instrument are shown. The heart of this spectrometer is a 40 W Mo or Rh anode micro-focus X-ray tube that can be interfaced to a monocapillary collimator or polycapillary lens, yielding X-ray beams in the range 20 μm to 3 mm. X-rays are detected with a 80 mm² Si(Li) detector. This instrument is available with a large vacuum chamber in which medium-sized artefacts (up to 25 × 20 × 9 cm³ in size) can be analysed without encountering practical problems.

![Fig. 4.32. Photograph of (a) the exterior and (b) the inside of the Eagle vacuum chamber, showing the positioning of an artefact on the motorized stage (shown retracted). By means of a camera, the interior can be observed when the vacuum chamber is closed.](image)
In general, the sensitivity of laboratory $\mu$-XRF setups is limited when compared to their synchrotron-based counterparts, as a result of the very large difference in primary intensity between regular X-ray tubes and synchrotron sources (Fig. 4.33). Provided appropriate spectrum collection times are employed (typically in the range 100–1000 s per point), relative detection limits in the range 20–50 ppm can be achieved (for transition elements in a glass matrix). This makes laboratory $\mu$-XRF instruments...
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significantly more suitable for the determination of low levels of the elements Ti-Mo in various materials than scanning electron microprobes.

A recent direction in μ-XRF instrument development is the construction of compact and/or portable small-beam instruments, consisting, e.g., of an air-cooled mini-focus X-ray tube, a compact optical element for beam focussing/collimation and a Peltier-cooled energy-dispersive detector. Such instruments, offering beams of 50–200 μm cross-section, are very useful for in situ investigations of archaeological and artistic materials, i.e., in the museum, gallery or archaeological site they are normally present.

In some cases, the spectrometer can be as simple as a compact X-ray tube equipped with a collimator tube, defining the X-ray beam to ca. 1–2 mm diameter, an optional beam filter and a small pin-diode detector attached to the side of the tube. Such a system can be very useful for in situ analysis of bronze statues [24,25]. Other systems make use of drift chamber detectors [26,27].

Bronk et al. [28] have described the design of a mobile spectrometer for μ-XRF with the requirements of archaeometry in mind. The ArtTAX instrument offers non-destructive and sensitive multi-elemental analysis, a sub-mm resolution with the possibility of working outside the laboratory. The spectrometer consists of an air-cooled, low-power molybdenum tube, a polycapillary X-ray lens that focuses the beam to ca. 100 μm, a silicon drift detector, a CCD camera, and three light diodes for sample positioning. The motor-driven measurement head is fixed on an x,y,z-flexible tripod support which can be assembled and dismantled within minutes. The detection limits of this device are in the range of 10 μg/g for transition elements in glass. Open helium purging in the excitation and detection paths enables the determination of elements down to sodium, thus avoiding vacuum conditions or a size-limiting sample chamber. To demonstrate the potential of ArtTAX in the field of art and archaeology, a selection of qualitative and quantitative results on pigment, metal, glass, and enamel analyses was presented [28].

Bichlmeier et al. [29,30] and Vittiglio et al. [31] have described another compact micro-XRF instrument, consisting of a similar set of compact components and applied it to the analysis of noble metals objects (such as coins, burial artefacts and statuettes in bronze and brass), multi-coloured beads and 20th century decorate glass objects and pigmented materials of various nature (18th century illuminated parch-ments various manuscripts from the 13th to the 19th centuries prepared with ferro-gallic ink.)
Synchrotron \( \mu \)-XRF instrumentation

In Fig. 4.34a the schematic layout of number of different \( \mu \)-XRF spectrometers that make use of synchrotron radiation are shown. The capabilities of some of these spectrometers is limited to elemental microanalysis while by means of other facilities, elemental analysis can be combined with other types of X-ray spectroscopy such as \( \mu \)-XANES and \( \mu \)-XRD.

*Polychromatic synchrotron \( \mu \)-XRF.* The experimental setup used for polychromatic synchrotron \( \mu \)-XRF measurements installed at Beamline L of the HASYLAB (Hamburg, Germany) synchrotron laboratory is schematically depicted in Fig. 4.34a.

*Figure 4.18a* shows the energy distribution in the white beam, produced in a bending magnet source, as seen through a \( 10 \times 10 \mu m^2 \) pin-hole, positioned at 20 m from the DORIS synchrotron ring. The bending magnets of this storage ring produce a white spectrum that contains appreciable

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K. Janssens

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Fig. 4.34. Schematics of (a) a polychromatic \( \mu \)-SRXRF spectrometer, (b) a combined \( \mu \)-SRXRF and \( \mu \)-XANES facility employing monochromatic excitation and (c) a confocal \( \mu \)-XRF excitation geometry, making use of pink-beam excitation. The setup shown in (d) is a monochromatic \( \mu \)-XRF/XRD facility at Beamlines ID18F and ID22, ESRF, Grenoble, France. Setups (a–c) are in operation at Beamline L, HASYLAB (DORIS III storage ring), Hamburg, Germany.
amounts of more energetic photons (above 60 keV), something which is not the case with many other synchrotron facilities, such as e.g., the National Synchrotron Light Source (NSLS, Upton, NY, USA).

The beam that originates from the storage ring is first collimated down to ca. 100 × 100 μm² by motorized cross-slits before entering a straight glass capillary. The latter is mounted onto a motorized $XY_{\theta}$-stage for alignment to the beam. Usually, straight borosilicate glass capillaries of inner diameter 10–50 μm are employed for micro-beam formation [32]; the capillary–sample distance is typically of the order of a few mm. The sample itself is mounted onto a motorized $XYZ_{\theta}$ stage, allowing it to be moved in increments.
of 1 μm and 0.1°, respectively. The sample surface plane is vertical and oriented at 45° to the incoming micro-beam and is also in the focal plane of the long-distance optical microscope, which is placed horizontally. Fluorescent signals are detected by a HPGe (high-purity germanium) solid-state detector; the latter is located at a distance of 5–7 cm from the sample and is shielded by a Ta/Pb enclosure. The detector collects the fluorescent and scattered radiations in a solid angle of ca. 0.001 steradians. The vertical position of the detector is such that it is exactly in the (horizontal) plane formed by the storage ring and the micro-beam. Since the HPGe detector is oriented at 90° to the micro-beam in the plane of maximum linear polarization, the XRF spectra which are collected in this way feature optimal peak-to-background ratios as the scatter-induced continuum background is reduced in intensity [33]. Behind the sample, an ionization chamber is placed to monitor the transmitted beam intensity; a similar monitor can be placed in the beam path between slits and capillary (not shown in Fig. 4.34a).

During conventional μ-XRF measurements, involving point analyses, line scans or two-dimensional (2D) mapping, the sample is moved through the beam by means of the motorized stage (in the XYZ directions) so that the appropriate locations on the surface are irradiated; the rotation stage (θ stage with vertically oriented rotation axis) normally is only useful during tomographic measurements [34]. Correlated stage movement and spectrum acquisition allows the collection of \( n_x \times n_y \) individual XRF spectra \( (n_x, n_y = \text{number of pixels in horizontal and vertical directions of the image}) \) which during or after the acquisition can be processed to yield (net) elemental maps, line profiles or area/phase-specific sum spectra of the irradiated material. By means of appropriate calibration models, the latter can be converted into quantitative images or local composition values [35]. The analytical characteristics of this facility are described more in detail elsewhere [36]. A special feature of this experimental facility is the fact that K-line XRF measurements can be performed on the elements ranging from K \((Z = 19)\) to Pb \((Z = 82)\) because of the high-energy components of the white beam. In the transition metal range, fg-level absolute detection limits in thin samples and ppm-level relative detection limits in thick organic or silicate-based samples are obtained while for the lanthanides, equivalent values are situated around 10 fg and 5–10 ppm, respectively, within 1000 s of irradiation time [37]. Next to the high intensity of the synchrotron beam, the high sensitivity over an extended element range is also the consequence of the fact that in SR–XRF spectra, a reduced background level is observed. This is the result of the polarized character of the radiation and the fact that the XRF is detected in the plane of the synchrotron ring (see Ref. [38] for
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details). A disadvantage of the use of the strongly penetrating primary and
fluorescent radiation is that the analytical signals in thick samples can
originate from extensive depths (e.g., for REE, this can be up to several mm
in glass samples), thereby reducing the effective lateral resolution of the
technique in one direction. This blurring effect can be avoided by employing
thin samples.

µ-XRF and µ-XANES using tunable monochromatic excitation. In the
setup shown in Fig. 4.34b, a narrow energy-band is selected from the
continuum by means of a fixed-exit Si(111) monochromator [39]. After
passing cross-slits, the monochromatic beam is demagnified by a polycapil-
lary lens. What is shown in Fig. 4.34b and c are so-called polycapillary half-
lenses, suitable for focussing of (quasi-parallel) synchrotron radiation. An
important feature of this type of lens is the large beam acceptance area,
typically several square millimetres in size. This permits to capture a large
fraction of the photons in the impinging beam, resulting in a high throughput
and gain factor. When the orientation of the monochromator crystals is kept
constant, µ-XRF measurements with monochromatic excitation can be
performed. This excitation form results in XRF spectra with very low
background levels, leading to relative detection limits situated in the 0.1–
10 ppm range and at the 0.1–1 fg level in thin samples. The increase in flux
density is of such a magnitude that it becomes possible to perform µ-XANES
measurements at a second generation synchrotron bending magnet source
where a very significant part of the initial beam is lost in the monochroma-
tization process [40,41].

Confocal µ-XRF and µ-XANES in monochromatic and pink-beam mode.
A striking difference between µ-XRF and micro-analytical methods such as
electron probe micro-analysis (EPMA), secondary ion microscopy (SIMS) and
laser-ablation inductively coupled mass spectrometry (LA-ICP-MS) is that
X-ray photons of sufficient energy can penetrate very deeply into the
material being analysed. Since this penetration depth can be one to several
orders of magnitude higher than the diameter of the focused X-ray beam,
often a degradation of the lateral resolution is observed [42,43] when samples
thicker than the beam size are investigated. In fact, rather than measuring
the lateral distribution of the elemental constituents at the surface of
the materials, a two-dimensional projection of the three-dimensional
distribution of these constituents in the sample is obtained.

This penetrative characteristic of X-ray beams is employed to advantage
in XRF tomography experiments, where through the measurement of a
series of the aforementioned projected distributions under various angles and
the use of appropriate mathematical back projection algorithms [44,45], it is
possible to perform three-dimensional elemental analysis in a non-destructive manner. Since this method involves rotation of the sample over 180° or 360° relative to the primary beam, it is limited to the investigation of relatively small objects, typically of dimensions of a few mm.

Figure 4.34c shows the same arrangement as that of Fig. 4.34a and b, but in this case, instead of one optical element (PC1, to focus the primary beam), a second optic (PC2) is placed between sample and detector. The polycapillary half-lens PC1 focuses (quasi-)parallel radiation that enters the wide end of the device into a focal spot that is situated ca. 5 mm outside the narrow end of the lens. Between the lens end and the focal spot, the resulting X-ray beam is strongly convergent, while after focus, it is strongly divergent. Around the focal spot, the primary X-ray beam has a narrow “waist”, as schematically shown in Fig. 4.35. At a primary energy $E_0$ of 21 keV, the diameter of the waist is ca. 10 μm. The narrow part of the waist extends in both directions for several hundreds of μm before significantly getting broader. Similarly, secondary radiation emitted by the sample atoms in the direction of the detector will pass through lens PC2 only when their point of origin is situated in the waist associated with PC2.

Thus, when the two lenses are situated perpendicular to each other in one plane, in such a way that the intersection of the two waists form a cube-like volume, only fluorescent signals generated in this volume will reach the detector. Within the limits imposed by (a) the absorption of the radiation in the sample and (b) the free distance to the end of the lenses, it is possible to arbitrarily position this micro-volume within the material being investigated. This method is henceforth denoted confocal μ-XRF. When combined with energy scanning, confocal μ-XANES measurements can also be performed in this arrangement. The spatial resolution obtained with such an arrangement

![Fig. 4.35. Detail of the intersecting waists of two polycapillary lenses aligned perpendicularly relative to each other in the same horizontal plane.](image)
is dependent on the energy of the primary and the fluorescent radiations being employed and is situated in the 10–40 μm range [46–48].

Since the introduction of the second lens before the detector causes the detected net count rate to decrease by a factor 10 or more, instead of using the highly monochromatic form of excitation required for XAS studies, “pink-beam” mode can also be employed. In this case, the Si(111) crystals of the monochromator are replaced by a pair of multilayer-coated reflectors. These reflectors select a relatively wide energy band (ΔE/E ≈ 10⁻²) out of the excitation spectrum (Fig. 4.18a), leading to a primary beam intensity that is ca. 30–50 times higher than in the case of monochromatic excitation.

Combined μ-SRXRF and μ-SRXRD at the ESRF ID22 and ID18F beamlines. ID18F and ID22 are undulator beamlines of the European Synchrotron Radiation Facility (ESRF), Grenoble, France. Instead of a continuous energy distribution, only photons within specific energy bands (undulator harmonics) are produced (see Fig. 4.18a). In Fig. 4.34d, a schematic of the experimental arrangement at ESRF ID18F is shown [49]. After the monochromator, the beam is focussed onto the sample by means of a CRL; an additional pin-hole is used to reduce the scatter background in the sample area and to define the beam in the horizontal direction. In this manner, beam sizes as small as 0.5 × 0.9 μm² can be obtained. Also with other optics, such as pairs of curved mirrors, beam sizes of these submicroscopic dimensions can be produced.

Next to energy-dispersive X-ray detector, at right angles to the primary beam, behind the sample, a wide angle XRD camera can be placed. This camera allows to record the diffracted beams generated in the sample up to a scattering angle 2θ of ca. 40°. By scanning a sample through the beam, simultaneously local composition information (from the generated XRF spectrum) as well as structural information (from the two-dimensional diffraction pattern) can be recorded.

4.3.3.6 Quantitative analysis

With the exception of TXRF, all forms of XRF analysis suffer from matrix effects, i.e., the observed net X-ray intensity of a specific element is not only a function of the concentration of the analyte element itself but also depends on that of the other constituents. This effect is caused by the absorption of X-rays in the sample and by fluorescence enhancements when the radiation is emerging from the sample. In samples with non-ideal homogeneity, the texture and size of the particles that constitute a porous sample may significantly influence the observed X-ray signals. Thus, in XRF very frequently curved rather than straight calibration
curves are obtained; only in case of the analyses of trace constituents in a constant matrix, in which the absorption and enhancement effects are constant or of very thin foil samples, in which no such non-linear phenomena occur, is the quantification of XRF signals relatively straightforward. The same applies to the quantification of TXRF data, where the equivalent of “thin” samples is being analysed.

Accordingly, a variety of correction and calibration models and procedures is in use in X-ray spectrometry based on (a) standard addition and dilution, (b) thin-film samples, (c) matrix dilution, (d) comparison to type standards, (e) internal standard elements and (f) mathematical corrections. A number of these procedures are destructive in nature (e.g., because they require dissolution of the material to be analysed) and therefore are not always applicable to analyses of cultural heritage materials. In these situations, the so-called “fundamental” approaches to the quantification problem in XRF are frequently employed. Here, knowledge on X-ray physics is employed to model all X-ray matter interactions in the sample in an attempt to correct for the matrix effects. Among the software packages that are available, a distinction can be made between those making use of (sometimes sophisticated) interpolation strategies between X-ray intensities derived from a large number of standard samples strongly resembling the unknown materials (e.g., a series of Cu-containing alloys when bronzes are analysed, a series of glass standards in the case of ceramics are studied) [50] or the software models that are based on a detailed knowledge of the XRF spectrometer response to different materials [51]. A more detailed treatment of quantification procedures is beyond the scope of this chapter.

4.3.4 XRD instrumentation

4.3.4.1 The Laue method
In the Laue method, polychromatic radiation is used to irradiate a single crystal that is stationary. The patterns that are recorded by means of photographic film, image plates or a CCD camera can be regarded as a stereographic projection of the planes of the crystal. Either a transmission or a back-reflection geometry is employed. Since the crystal is fixed in space, the interplanar distances \( d \) and the Bragg angle \( \theta \) is fixed for every set of planes in the crystal. The only possible variations are the diffraction order \( n \) and the wavelength \( \lambda \). Thus, the diffracted beams form arrays of spots that lie on curves on the film. Each set of planes picks out and diffracts the particular wavelength from the white radiation that
satisfies the Bragg law for the values of $d$ and $\theta$ involved. Each curve therefore corresponds to a different wavelength. The spots lying on any one curve are reflections from planes belonging to one zone. Laue reflections from planes of the same zone all lie on the surface of an imaginary cone whose axis is the zone axis.

In the back-reflection Laue arrangement (see Fig. 4.36a), the film is placed between the X-ray source and the crystal. The beams that are diffracted in a backward direction are recorded. One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on a hyperbola. In the transmission Laue method (Fig. 4.36b), the film is placed behind the crystal to record beams that are transmitted through the crystal. As before, one side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an ellipse.

Fig. 4.36. The Laue method in (a) back-reflection geometry and (b) transmission geometry.
Crystal orientation is determined from the position of the spots. Each spot can be indexed, i.e., attributed to a particular plane, using special charts. Greninger charts are used for back-reflection patterns and Leonhardt charts for transmission patterns. The Laue technique can also be used to assess crystal perfection from the size and shape of the spots. If the crystal has been bent or twisted, the spots become distorted and smeared out.

4.3.4.2 Powder diffraction

When a monochromatic beam of wavelength $\lambda$ is directed at a single crystal, then only one or two diffracted beams may result (Fig. 4.37a). When the crystal is now rotated around the impinging beam so that the

![Diffraction Diagram]

Fig. 4.37. The powder method. Irradiation of (a) a single crystal results in one or a few reflections and (b) a powdered sample results in cones of diffracted radiation which can be recorded on film (c).
angle between the diffracting planes and the primary beam remains the same, then the reflected beam will describe a cone with the crystal at its apex. The same effect can be obtained when instead of rotating a single crystal, the irradiated material consists of hundreds to thousands of very small crystals, all having a random orientation of their own. The diffracted beams are seen to lie on the surface of several cones. The cones may emerge in all directions, forwards and backwards, as illustrated in Fig. 4.37b. A circle of film can be used to record the diffraction pattern as shown in Fig. 4.37c. Each cone intersects the film, giving rise to arcs on the film. For every set of crystal planes, by chance, one or more crystals will be in the correct orientation to give the correct Bragg angle to satisfy Bragg’s equation. Every crystal plane is thus capable of diffraction. Each diffraction line is made up of a large number of small spots, each from a separate crystal. Each spot is so small as to give the appearance of a continuous line. If the crystal is not ground finely enough, the diffraction lines appear speckled.

This is the basis of the Debye-Scherrer or powder method of XRD; it is probably the most commonly applied method in X-ray crystallography. The powder method is used to accurately determine the value of the lattice parameters (the magnitude of the unit cell vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$) of a crystal.

In practice, the powder camera consists of a metal cylinder at the centre of which is placed the sample (see Fig. 4.38). Powdered material is typically glued to a glass rod with an amorphous type of adhesive. A strip of X-ray film is placed inside the cylinder with two holes punched into it: one for the
primary beam to enter the camera and a second for the beam to stop, diametrically opposed to the first. The camera enclosure is light-tight and placed in front of the X-ray beam.

A typical Debye-Scherrer pattern obtained with this type of camera is shown in Fig. 4.37c.

4.3.4.3 The rotating crystal method

In the rotating crystal method, a single crystal is mounted on an axis normal to a monochromatic X-ray beam. A cylindrical film is placed around it and the crystal is rotated about the chosen axis. As the crystal rotates, sets of lattice planes will at some point make the correct Bragg angle for the monochromatic incident beam, and at that point a diffracted beam will be formed. Since the reflected beams are located on the surface of imaginary cones, their intersections with the film (after flattening) are horizontal lines, as shown in Fig. 4.39a. The main use of the rotating crystal method is in the determination of unknown crystal structures. The precession, oscillation, and Weissenberg methods use variations of this theme.

The Gandolfi camera. When confronted with phase identification problems in the field of art and archaeometry, an additional difficulty may be the fact that only very small samples (if any) are available for analysis. Sample may be tiny single crystals or agglomerates of a few single crystals. The Gandolfi XRD camera allows non-destructive analysis of single crystals smaller than 100 μm in diameter via the recording of a “powder pattern”. In this device, a single grain or crystal is doubly rotated in the X-ray beam in order to sequentially expose all available atomic planes to diffracting positions. A schematic of the Gandolfi camera is shown in Fig. 4.40.

![Diagram](image_url)

Fig. 4.39. The crystal rotation method: (a) general arrangement, (b) detail of the crystal mounting head.
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Fig. 4.40. Photograph (left) and schematic (right) of the Gandolfi camera. The diffracted beam hits the film at \( R \). The angle \( \chi \) (which can be freely chosen in a 4-circle diffractometer) is fixed at 45° while the specimen rotates about the \( \Omega \) and \( \Phi \) axes.

It closely resembles a Debye-Scherrer camera. The sample is mounted on the tip of a needle that is mounted at 45° to the camera axis \( \Omega \). The needle rotates around its own axis (\( \Phi \)-rotation) as well as around the camera axis. Requiring a sample barely visible to the naked eye, this technique is capable of identifying the mineral constituents of minute samples of paint used, e.g., by prehistoric artists or applied in very thin layers by easel painters. Recently, a Gandolfi camera equipped with an image plate detector has been developed [52].

**Diffractometers.** Of many of the XRD instruments described above that make use of X-ray film, more modern equivalents are available that either use imaging plates (i.e., laser readable and erasable X-ray-sensitive surfaces), X-ray-sensitive CCD cameras or Geiger/scintillator counters as X-ray detectors. The latter are normally mounted on computer-controlled and commercially available 4-circle diffractometers (see Fig. 4.41) that only require the crystal to be aligned in the X-ray beam; the instruments’ software will autonomously measure and refine unit-cell dimensions, record all reflections out to a maximum \( \theta \)-angle and store their intensities.

**4.3.4.4 Quantitative XRD analysis: Rietveld refinement**

A drawback of the conventional method of powder diffraction is that the XRD patterns of the constituent phases of a mixture strongly overlap, thereby preventing proper determination of the structure and/or its the quantitative analysis of the mixture. In the 1960s, Rietveld [53,54] developed a method to effectively separate the individual constituent of an unknown XRD pattern from each other in a quantitatively reliable manner, thereby allowing an accurate determination of the structure. By fitting the experimental data to a (relatively simple) model, sample
properties (such as the particle size distribution, the preferred orientation of grains, lattice constants, site occupancies, etc.) and a number of instrumental effects that influence the recorded diffraction patterns (such as the variation of the peak widths with diffraction angle, the type of X-ray tube, the slit settings, the goniometer radius, the polarization of the radiation, etc.) can be accounted for. In such circumstances, quantitative XRD analysis becomes equivalent to multiple linear regression of unknown XRD patterns (of mixtures of phases) against a library of patterns of single constituents. For reliable quantitative analysis of powders, however, it is essential that two conditions be fulfilled: (a) samples must be carefully prepared to comply to the definition of a powder: they must be homogeneous and a sufficient number of particles with random orientation must be present and (b) the structure factors of the constituents must be correctly calculated. In complex materials, as encountered in the cultural heritage area, especially condition (a) is not always fulfilled, which may limit the reliability of the analysis results (Fig. 4.42).

In general, however, the Rietveld refinement approach has been so successful that nowadays the structure of materials, in the form of powders, is routinely being determined with a comparable accuracy as obtained by means of single crystal diffraction techniques [55]. Rietveld refinement is widely used for quantitative phase analysis, resulting yearly in more than a thousand scientific papers applying it [56].
4.3.5 XAS instrumentation at SR beamlines

As already explained above, for most XAS experiments, highly monochromatic synchrotron radiation is required. The degree of monochromaticity is usually expressed as a relative energy width $\Delta E/E$, which typically is of the order of $10^{-4}$ (i.e., $\Delta E = 1$ eV at $E = 10$ keV) in case the Si(111) reflection is used for monochromatization.

Fig. 4.42. Left panel: (a) car paint multilayer stack, consisting of a series of nine (possibly 10) differently pigmented or transparent layers with thicknesses in the range 20–100 μm; right panel: X-ray intensity depth profiles of various elements. The sample was analysed with the blue layer on top. Layer 1 (blue) can be observed to contain Ti, some Co, Cu and Pb; layer 2 (red) contains Cr, Fe, Cu, Zn and some Sr; layer 3 (black) is not associated with any strong XRF intensity; layer 4 (orange) contains Ti, Fe, Co and Zn, but less Fe and more Zn than layer 2; layers 5–7 (black) also do not show strong XRF signals, except layer 6 that is associated with Sr and some Co; finally layer 8 (orange) shows a similar pattern as layer 4. Some of the signals originating from this deep layer (ca. 350 μm deeper than the surface) are strongly absorbed by the layers on top of it. Layer 9 is a transparent varnish layer.

(For a colored version of this figure, see Plate 4.I, page 791.)
It is the most basic form, a double crystal monochromator consisting of two parallel crystals mounted on a common rotation table so that the diffraction angle $\theta$ can be continuously varied (see Fig. 4.34b and c). The first crystal selects the wavelength (and its higher order overtones) while the diffraction at the second crystal ensures that the monochromatic beam regains a horizontal direction. In between the sample and the monochromator, X-ray focusing optics of various types can be placed in order to concentrate the X-ray beam in the horizontal and/or vertical direction. If the beam is focused to dimensions below ca. 100 $\mu$m, the use of a fixed-exit monochromatic is recommended, to ensure that the focused beam spot does not change in size and position during energy scans. The experimental setup shown in Fig. 4.34b allows to simultaneously record XAS data in two manners:

**Absorption XAS.** The most straightforward mode of operation is to directly record the intensity of a monochromatic beam before and after (a homogeneous) sample as a function of energy $E$ by means of two ionization chambers (see ION1 and ION2 in Fig. 4.34b and c) and calculate the $\mu(E)$ vs. $E$ curve:

$$\ln\left(\frac{I(E)}{I_0(E)}\right) = -\mu(E) \cdot \rho \cdot d$$

(4.15)

where the sample areal density $\rho \cdot d$ is a scaling factor that usually is normalized out.

An ionization chamber essentially consists of two isolated parallel metal plates between which a voltage (several 100 V) is applied. The electrical current flowing between the two condenser plates is proportional to the flux $I$ of the X-ray beam that passes in between. XAS data with sufficiently signal-to-noise ratio can be obtained when (a) the absorption in the sample is not too large so that $I(E)$ and $I_0(E)$ do not differ too much and (b) the concentration of the absorbing element is high enough (>0.1% w/w) so that a significant difference between $I(E)$ and $I_0(E)$ can be recorded.

**Fluorescent XAS.** When the sample under investigation is so strongly absorbing (or so thick) that the transmitted intensity is no longer measurable or when XAS data from a minor/trace constituent are to be recorded, instead of directly measuring the absorption, one of the signals produced as a result of photoelectric absorption can be recorded as a function of the primary energy. By means of the energy-dispersive detector, positioned at 90° to the primary beam (see Fig. 4.34b and c), the fluorescence intensity profile $I_{fl}(E)$ vs. $E$ can be recorded. When the absorbing element is not too strongly concentrated (<0.1–0.5%), the normalized fluorescent intensity $I_{fl}(E)/I_0(E)$ is proportional to $\mu(E)$, provided appropriate dead-time corrections, etc., are
X-ray based methods of analysis

taken into account. An alternative to detection of the fluorescent intensity is to record the total electron yield (TEY), i.e., to measure the number of (photo)electrons emitted by the sample during the irradiation as a function of the primary beam energy $E$. The TEY mode of detection is especially useful at low primary energies and when low atomic number elements are studied.

4.4 A SURVEY OF APPLICATIONS OF X-RAY METHODS IN THE CULTURAL HERITAGE SECTOR

Synchrotron ($\mu$-)XRF, offering (sub)ppm level detectability for many elements [57] on the basis of the irradiation of minute samples, can be used for detailed and quantitative finger-print analysis of materials in order to gain a better understanding on their provenance. The use of a microscopic X-ray beam of monochromatic energy also permits the detailed investigation of the processes that have altered the surface composition of a material, through the use of XRF, XRD or XAS.

Though suitable for trace-level micro-analysis of organic materials (e.g., paper, pigments dispersed in a organic binder) or of silicate-rich materials such as pottery or glass, the high primary intensity of synchrotron micro-beams usually is not compatible with the XRF analysis of metallic materials (e.g., artefacts made in bronze, iron, silver, gold or alloys of these metals).

Laboratory $\mu$-XRF can be conveniently used for this purpose. Another strong point of laboratory $\mu$-XRF is the possibility to perform local (quantitative) analysis on objects whose size, shape or nature is incompatible with the vacuum and the small sample enclosures employed by most conventional micro-analytical techniques such as EPXMA and $\mu$-PIXE. In this respect, $\mu$-XRF offers similar possibilities to external-beam PIXE [2] (see also Chapter 5), but in some cases with a better lateral resolution.

Even for smaller objects (such as, e.g., coins), which might be analysed as a whole in conventional XRF apparatus, the use of a small beam instrument offers advantages. A small X-ray beam permits to analyse an object at various locations, e.g., to verify that all parts of a statue are made of the same material, or to investigate the homogeneity of the material used. XRF on curved or otherwise non-flat surfaces can lead to errors in the quantification (especially for metallic materials) [58]; with a small beam, it is in general easier to select locations on an object that more closely resemble the ideal, flat and polished surface normally required for reproducible quantitative measurements. In case corroded objects are under investigation, only a small area of the (altered) surface needs to be removed in order to expose the underlying original material.
In what follows, after briefly describing the instrumentation employed for the investigations, a limited number of case studies highlighting the above-outlined types of investigations are outlined. Depending on the nature of the investigation and the type of information required, one of the various forms of X-ray analysis described above may be employed. In several books [59–61] and special journal issues [62], several other collections of similar case studies can be found.

4.4.1 Compositional analysis of historic Glass

The composition of glass, produced from prehistoric to the modern ages, has been subject to a number of distinct changes, depending on the raw materials available and the state of glass-making technology and know-how. Thus, chemical analysis of excavated glass fragments can be very useful for gaining information on glass-making technology and/or glass trade in different periods. X-ray-based methods have been used extensively for analysing this type of material [63–68], next to other (trace-level) methods of (micro-)analysis [69–71], as detailed in Chapter 15.

4.4.2 Pigments

Essentially two X-ray-based approaches to pigment analysis in painted works of art (oil paintings, frescoes, miniatures and illuminated manuscripts) can be distinguished: (a) the in situ approach where portable equipment is employed to irradiate a small part of a large artefact and (b) the ex situ approach where the pigmented layer(s) to be examined are sampled with minimal damage to the work of art and the resulting minute fragments or particles are examined by means of one or more techniques in specialized laboratories. For the detailed characterization of paint layer stratigraphies, traditionally small fragments are removed from oil paintings by means of a hollow needle or a fine scalpel. However, as outlined below, such a destructive procedure is not always necessary.

The pallet of inorganic pigments contains a wide range of different types with well-known chemical compositions (see Table 4.6). Inorganic pigments have been used for all colours of the artists’ pallet because of their high colouring power and their stability against changes in temperature, climate and light. Each inorganic pigment is characterized by its colour and by one or more constituting elements; when these key-elements are observed in the correct proportions, the pigment can be identified. Furthermore impurities can give information on the provenance and/or manner of manufacture of
<table>
<thead>
<tr>
<th>Colour</th>
<th>Pigment name</th>
<th>Chemical composition</th>
<th>Key element(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>White</td>
<td>Antimony white</td>
<td>Sb₂O₃</td>
<td>Sb</td>
</tr>
<tr>
<td></td>
<td>Lithophone</td>
<td>ZnO + BaSO₄</td>
<td>Zn, Ba</td>
</tr>
<tr>
<td></td>
<td>Permanent white</td>
<td>BaSO₄</td>
<td>Ba</td>
</tr>
<tr>
<td></td>
<td>Titanium white</td>
<td>TiO₂</td>
<td>Ti</td>
</tr>
<tr>
<td></td>
<td>White lead</td>
<td>2PbCO₃·Pb(OH)₂</td>
<td>Pb</td>
</tr>
<tr>
<td></td>
<td>Zinc white</td>
<td>ZnO</td>
<td>Zn</td>
</tr>
<tr>
<td></td>
<td>Zirconium oxide</td>
<td>ZrO₂</td>
<td>Zr</td>
</tr>
<tr>
<td></td>
<td>Chalk</td>
<td>CaCO₃</td>
<td>Ca</td>
</tr>
<tr>
<td></td>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>Ca</td>
</tr>
<tr>
<td>Yellow</td>
<td>Auripigmentum</td>
<td>As₂S₃</td>
<td>As</td>
</tr>
<tr>
<td></td>
<td>Cadmium yellow</td>
<td>CdS</td>
<td>Cd</td>
</tr>
<tr>
<td></td>
<td>Chrome yellow</td>
<td>2PbSO₄·PbCrO₄</td>
<td>Cr</td>
</tr>
<tr>
<td></td>
<td>Cobalt yellow</td>
<td>K₃[Co(NO₂)₆]·1.5H₂O</td>
<td>K, Co</td>
</tr>
<tr>
<td></td>
<td>Lead-tin yellow</td>
<td>Pb₂SnO₄/PbSn₁₋ₓSₓO₇</td>
<td>Sn</td>
</tr>
<tr>
<td></td>
<td>Massicot</td>
<td>PbO</td>
<td>Pb</td>
</tr>
<tr>
<td></td>
<td>Naples yellow</td>
<td>Pb(SbO₃)₂/Pb(SbO₄)₂</td>
<td>Pb, Sb</td>
</tr>
<tr>
<td></td>
<td>Strontium yellow</td>
<td>SrCrO₄</td>
<td>Sr, Cr</td>
</tr>
<tr>
<td></td>
<td>Titanium yellow</td>
<td>NiO·Sb₂O₃·20TiO₂</td>
<td>Ni, Sb, Ti</td>
</tr>
<tr>
<td></td>
<td>Yellow ochre</td>
<td>Fe₂O₃·nH₂O (20–70%)</td>
<td>Fe</td>
</tr>
<tr>
<td></td>
<td>Zinc yellow</td>
<td>K₂O·4ZnO·4CrO₃·3H₂O</td>
<td>Zn, Cr</td>
</tr>
<tr>
<td>Red</td>
<td>Cadmium red</td>
<td>CdS + CdSe</td>
<td>Cd, Se</td>
</tr>
<tr>
<td></td>
<td>Cadmium vermilion</td>
<td>CdS + HgS</td>
<td>Cd, Hg</td>
</tr>
<tr>
<td></td>
<td>Chrome red</td>
<td>PbO·PbCrO₄</td>
<td>Pb, Cr</td>
</tr>
<tr>
<td></td>
<td>Molybdate red</td>
<td>7PbCrO₄·2PbSO₄·PbMoO₄</td>
<td>Pb, Cr, Mo</td>
</tr>
<tr>
<td></td>
<td>Realgar</td>
<td>As₂S₃</td>
<td>As</td>
</tr>
<tr>
<td></td>
<td>Red lead</td>
<td>Pb₂O₄</td>
<td>Pb</td>
</tr>
<tr>
<td></td>
<td>Red ochre</td>
<td>Fe₂O₃ (up to 90%)</td>
<td>Fe</td>
</tr>
<tr>
<td></td>
<td>Vermilion</td>
<td>HgS</td>
<td>S, Hg</td>
</tr>
<tr>
<td>Green</td>
<td>Basic copper sulphate</td>
<td>Cu₄(SO₄)₃(OH)₂</td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td>Chromium oxide</td>
<td>Cr₂O₃</td>
<td>Cr</td>
</tr>
<tr>
<td></td>
<td>Chrysocolla</td>
<td>CuSiO₃·nH₂O</td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td>Cobalt green</td>
<td>CoO·5ZnO</td>
<td>Co, Zn</td>
</tr>
<tr>
<td></td>
<td>Emerald green</td>
<td>Cu(CH₃COO)₂·3Cu(AsO₂)₂</td>
<td>Cu, As</td>
</tr>
<tr>
<td></td>
<td>Guignent green</td>
<td>Cr₂O₃·nH₂O + H₃BO₃</td>
<td>Cr</td>
</tr>
<tr>
<td></td>
<td>Malachite</td>
<td>CuCO₃·Cu(OH)₂</td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td>Verdigris</td>
<td>Cu(CH₃COO)₂·nCu(OH)₂</td>
<td>Cu</td>
</tr>
</tbody>
</table>

continued
specific colouring materials. Since the chronological use of most pigments is known, it is possible in some cases to determine an approximate date for the genesis of painted historical objects. Due to the circumstance that some pigment appeared on artists’ pallets after a certain time (post quem) or another pigment disappeared before that time (ante quem), it is possible to distinguish between original materials, restored parts or fakes [20,72].

However, a number of problems render pigment identification by means of XRF or X-ray emission analysis alone difficult. A first difficulty derives from the fact that, as is apparent from Table 4.6, many pigments share key elements (e.g., the presence of the element Sb may point to the presence of antimony white or to that of Naples Yellow, that of Cu to many green or blue pigments) so that the observation of a specific element in the XRF spectrum cannot always be used as an unambiguous indication of the presence of a specific pigment. Especially in the case of Cu-containing greens and Fe-containing yellow-browns, the data provided by XRF or emission analysis are rather unspecific. A second problem has to do with the fact that during X-ray irradiation of artefacts that have been covered with more than one pigmented layer (e.g., varnish, ground and support layers next to one or more actual paint layers), the constituents of many (if not all) of these layers will contribute to the observed XRF spectrum. Strong X-ray lines of,
e.g., a lead-white base layer may then obscure much weaker X-ray lines of the top-most layers while generally the interpretation becomes more cumbersome. Similarly, when pigments are mixed to obtain a particular colour, the identification of the individual components can be rendered more difficult. In quite a few cases, however, the identification is unproblematic and the XRF method can even be used to determine the mixing ratio(s) of the original pigments. In other cases, specific measures need to be taken to either (a) increase the specificity of the analysis or (b) limit the depth in the paint layer stack from which the signals in the XRF spectrum originate.

The use of compact portable XRF equipment for pigment identification has been described predominantly for the analysis of frescoes and ceramics [25,73]. With these works of art, usually a single pigmented layer covers a substrate material so that most of the observed XRF signals can straightforwardly be attributed to constituents of the coloured layer. In some cases, however, also with frescoes, complicated stratigraphies can be encountered. For example, during the study of the frescoes of Giotto in the Chapel of the Scrovegni in Padova, Italy [74], it could be established by means of portable XRF and without any sampling that the golden haloes in these frescoes are composed of different layers: (a) a superficial layer of calcium sulphate, due to pollution, (b) a (on average) 1.6 μm thick layer of gold leaf, (c) a Cu-containing glue layer, having an equivalent Cu thickness of 1 μm, (d) a layer of white lead, having an equivalent Pb thickness of around 5 μm, (e) possibly a layer of azurite (Cu) and finally (f) the Fe- and Sr-containing plaster substrate. Bronk et al. [28] have used the ArtAX spectrometer for studying the evolution of the use of pigments in enamelled objects of the 16th–19th century where, e.g., the occurrence of Ni, As and Bi impurities in Co-blue enamels is indicative of a 16–17th dating of the objects while the absence of the former elements is observed in Co-blue enamel layers of objects (re)produced in the 19th century.

In Chapter 14, the use of TXRF for analysis of minuscule amounts of pigments, removed from illuminated manuscripts by a virtually non-destructive sampling method, is discussed in greater detail. By means of this method, pigments from the top-most pigmented layer of (oil) paintings can be analysed, provided the varnish layer is removed (e.g., during restoration activities).

Analysis of paint multilayers by means of the confocal variant of μ-XRF is relatively new possibility which shows a lot of promise for application in the cultural heritage sector [48]; preliminary experiments on car paint multilayers, consisting of up to 9 different coatings showed that each layer could be non-destructively analysed separately (see Fig. 4.41). This method was also
demonstrated to be applicable to quantitative analysis of complex paint layers stratigraphies encountered in 16th century oil paintings [75].

4.4.3 Lustre ware

Pottery from the Middle Ages and Renaissance Era often is decorated with glazes showing gold and copper-coloured metallic reflections and iridescence. These effects are called lustre and consists of a metal deposition on a tin-opacified lead glaze that produces the brilliant metallic reflections of different colour and iridescence [77].

The technique of lustre was developed by the Islamic culture in Mesopotamia, during the 9th century AD. Since muslims were not allowed to use gold in artistic representations, a way was found to create the same effect without using real gold. It arrived in Spain during medieval times, following the expansion of Arabian culture. From there it was introduced into the centre of Italy, where it was exploited to produce polychrome lustre Renaissance pottery. Thus, lustre became one of the most important decorative techniques of the Medieval and Renaissance pottery of the Mediterranean basin.

Centuries later, the lustre is still visible thanks to the high quality of the film and its resistance to atmospheric oxidation and burial weathering. The specific optical properties of the films are the consequence of the presence of silver and copper nanoparticles, dispersed homogeneously in the glassy matrix of the ceramic glaze. To create these nanoparticles, artisans applied a mixture of copper and silver salts and oxides, together with vinegar, ochre and clay, on the surface of previously glazed pottery. The object was then placed in a kiln for heating to about 600°C in a reducing atmosphere. The high temperature caused the glaze to soften so that copper and silver ions could migrate into the outer layers of the glaze. In the reducing atmosphere, the ions reduced to metals, which upon aggregation formed nanoparticles that gave rise to the desired colour and optical properties. Different recipes were used to obtain different lustre colours, ranging from goldlike to copperlike. A red originates from the migration of copper ions and their subsequent reduction. In the case of gold shades, in principle only silver is needed, but craftsmen used both copper and silver. Researchers are still trying to find out why they used both materials and what procedure was employed, since copper needs higher temperatures than silver in order to stimulate the formation of nanoclusters. The lustre technique shows that craftsmen had an advanced technological and empirical knowledge of material science.
Several techniques have been used to characterize the chemical and physical properties of these films. Detailed compositional information can be obtained by Rutherford Backscattering Spectrometry (RBS, see Chapter 5), while the optical properties can be investigated by optical absorption in the visible–ultraviolet region. By electron microscopy (TEM and SEM) it was possible to visualize the metallic particles present in the glaze; silver and copper nanocrystals can be well separated in TEM pictures. They are quasi-spherical, with a diameter between 5 and 100 nm. Silver nanocrystals, larger than copper ones, appear grouped together among copper crystals and close to the glaze surface.

From XRD patterns, the crystalline phase of the particles could be derived. In order to determine the valence state of Ag and Cu and to describe the local atomic environment around the metallic species, XAS measurements were performed. These permitted to study the amorphous oxide phase in which the metals are present. Lustre samples of glazed Renaissance pottery (end of XV–XVI century) from Deruta and Gubbio, Italy were analysed [78]. Examples of lustre pottery from these localities are on display in many important international museums, such as the Louvre Museum (Paris, France) and the Metropolitan Museum of Art, New York, USA. The lustre on the examined artefacts consists of a heterogeneous metal–glass composite film, some hundreds of nanometres thick, analogous to that present in the modern metal–glass nanostructured composites synthesized for high-technology applications [79,80]. It was found that in the case of red lustre, the colour was mainly due to the presence of copper nanoclusters, while in the case of gold lustre the colour was caused by nanoclusters of silver. In the gold lustre, Ag\(^{+}\), Cu\(^{+}\) and Cu\(^{2+}\) ions are present, while in the red lustre, according to the historical recipes [81,82], the dominant ion is Cu\(^{+}\). The nanoclusters are confined to the more external glaze while the oxidized forms are present at larger depths.

**Figure 4.43** summarizes some of the XANES results obtained at the Cu-K edge (8979 eV). When XANES data are recorded in the fluorescence mode of detection, where the lustre layer is probed down to a depth of 50 \(\mu\)m, Cu appears to be predominantly present under an oxidized form (i.e., as Cu\(^{+}\) in Cu\(_2\)O, cuprite). However, if the TEY mode of detection is used, where only the top 100 nm of the same lustre layer is analysed, a different profile is obtained, showing the presence of Cu in the metallic state.

The analysis of the EXAFS spectra obtained for three red lustre samples, performed in fluorescence mode, suggests the presence of copper coordinated by oxygen atoms at a distance of 1.86 \(\AA\), which is a distance very close to the
distance for the first shell of Cu$_2$O (1.85 Å). The Cu–O first shell coordination also shows a number of neighbours not very far from 2, the value shown by the Cu$_2$O standard.

In general, one can state that the chemical state and local environment of the Cu ions are similar to those found in copper–alkali ion-exchanged silicate glass samples. This finding strongly supports the view that lustre formation is mediated by a copper- and silver–alkali ion exchange as a first step, followed by nucleation and growth of metal nanocrystals as a spontaneous process due to the supersaturation of the elemental concentrations in the region where clustering occurs.

### 4.4.4 Metallic artefacts

COPRA, short for “Compact Röntgen Analyser”, is a fully equipped micro-XRF instrument intended for easy transportation to musea and galleries. Bichlmeier et al. [83] have used this instrument for the analysis of five golden medallions and two Roman coins (dated 550–575 AD) that were all fitted with small attachment rings (Fig. 4.44). The questions regarding these artefacts were the elemental composition of the rings and medallions and whether different or identical gold alloys could be identified. The average compositions of the artefacts’ rear sides and rings were obtained from three measurements on different spots (Table 4.7). The standard deviations of the Cu, Ag and Au concentrations were 2–8%. This relatively small uncertainty
allowed the grouping of identical artefact and ring materials according to their compositions.

For example, the prominent high silver content of medallions M4 and M5 leads to the conclusion that both belong to one group; also, their composition of gold and copper match well. The composition of the bulk materials can be combined easily with the shape of the objects: Both Roman coins (Fig. 4.44, Nos. 3 and 6), the two smaller medallions with a convex projection (Fig. 4.44, Nos. 4 and 5) and the three richly ornamented, large medallions (Fig. 4.44, Nos. 1, 2 and 7) consist of the same material. Also, the attached rings of the larger medallions and the Roman coins show identical compositions. The standard deviations of the copper, silver and gold

![Fig. 4.44. Series of seven late-Roman gold medallions, fitted with attachment rings.](image)

<table>
<thead>
<tr>
<th>% w/w</th>
<th>Back side</th>
<th></th>
<th></th>
<th></th>
<th>Ring</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Cu</td>
<td>Ag</td>
<td>Au</td>
<td>Fe</td>
<td>Cu</td>
<td>Ag</td>
<td>Au</td>
</tr>
<tr>
<td>M1</td>
<td>1.0</td>
<td>0.5</td>
<td>8.6</td>
<td>90.1</td>
<td>1.5</td>
<td>1.3</td>
<td>8.3</td>
<td>88.8</td>
</tr>
<tr>
<td>M2</td>
<td>0.3</td>
<td>0.6</td>
<td>8.7</td>
<td>90.3</td>
<td>1.0</td>
<td>1.4</td>
<td>6.7</td>
<td>91.1</td>
</tr>
<tr>
<td>M3</td>
<td>1.5</td>
<td>0.4</td>
<td>1.2</td>
<td>96.9</td>
<td>0.9</td>
<td>2.4</td>
<td>8.6</td>
<td>88.0</td>
</tr>
<tr>
<td>M4</td>
<td>0.3</td>
<td>1.8</td>
<td>18.7</td>
<td>79.4</td>
<td>0.3</td>
<td>1.8</td>
<td>15.2</td>
<td>82.9</td>
</tr>
<tr>
<td>M5</td>
<td>0.3</td>
<td>1.7</td>
<td>18.4</td>
<td>79.6</td>
<td>0.2</td>
<td>2.0</td>
<td>15.0</td>
<td>83.0</td>
</tr>
<tr>
<td>M6</td>
<td>0.2</td>
<td>0.5</td>
<td>1.4</td>
<td>98.1</td>
<td>1.4</td>
<td>1.5</td>
<td>8.3</td>
<td>88.2</td>
</tr>
<tr>
<td>M7</td>
<td>1.4</td>
<td>0.6</td>
<td>8.1</td>
<td>90.3</td>
<td>8.5</td>
<td>3.0</td>
<td>8.8</td>
<td>79.9</td>
</tr>
</tbody>
</table>
concentrations were fairly small (2–8%), while the standard deviation of the iron concentration was about 40%. A possible explanation is that iron particles may have been introduced mechanically into the artefacts (e.g. by hammering) and therefore are distributed inhomogeneously. For this reason, the iron concentration was not considered further. For the gold artefacts it was assumed that the rings of medallions 1 and 2 were attached in the manufacturing process, whereas medallion 7, which shows distinct signs of mending, was repaired subsequently. The mounting of rings on the Roman coins took place in a second step of production, since the material of the bulk and of the eye do not have the same composition. This implies that the coins originally used as currency were transformed into pendants and not manufactured in one piece. There were no apparent distinctions between the rings and medallions M4 and M5, so that it was not possible to determine if the rings were attached originally or subsequently. It was possible to distinguish different ring materials: those of medals M4 and M5 show the same composition, and also M1, M2, M3 and M6. Owing to this grouping it can be assumed that medallions M1 and M2 were made from the same material and therefore in the same workshop where coins M3 and M6 were modified. In Chapter 12, the analysis of coins for elucidating their provenance is discussed in greater detail.

The above-described studies concerned investigations of materials that could either be sampled or the complete object could be easily brought into the laboratory. Sometimes, however, the analytical instrument must be brought to the objects. During an exhibition of ancient gold artefacts from the Iranian National Museum in the Kunsthistorisches Museum (Vienna, Austria), a number of these valuable items were analysed on site by means of the COPRA instrument. The complete setup of the instrument took ca. 45 min. Five objects were analysed in various places with the aim of determining the type of gold alloy they were manufactured from and in order to document possible difference in origin of these objects. The spectral data were calibrated against a series of Au/Ag/Cu standards (Ögussa, Austria). The average compositions are summarized in Table 4.8. Quasi-straight line calibration curves between observed X-ray intensities and the concentration of the above-mentioned elements were established. Since it concerns a metallic matrix, the obtained concentration data was normalized to 100%. Three of the objects are made in fine gold (pure Au with some Cu present) while two others are made in different Au/Ag/Cu alloys. The variability of the composition within most objects was small. In Fig. 4.45, a photograph taken during the irradiation of one of the artefacts (a griffin) is shown. In this case, the object is positioned before the X-ray beam by means of a manual
X-ray based methods of analysis

### TABLE 4.8

<table>
<thead>
<tr>
<th>Object</th>
<th>Number of analysis points</th>
<th>Au (%)</th>
<th>Ag (%)</th>
<th>Cu (%)</th>
<th>Other lines (not quant.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lion</td>
<td>18</td>
<td>98.8</td>
<td>0.0</td>
<td>1.2</td>
<td>Fe</td>
</tr>
<tr>
<td>Griffin</td>
<td>8</td>
<td>99.0</td>
<td>0.0</td>
<td>1.0</td>
<td>Fe</td>
</tr>
<tr>
<td>Bracelet</td>
<td>9</td>
<td>99.2</td>
<td>0.0</td>
<td>0.8</td>
<td>K, Ca, Fe</td>
</tr>
<tr>
<td>Beaker</td>
<td>3</td>
<td>64.8</td>
<td>31.7</td>
<td>3.4</td>
<td>Fe</td>
</tr>
<tr>
<td>Seal</td>
<td>5</td>
<td>83.6</td>
<td>12.4</td>
<td>4.0</td>
<td>Fe</td>
</tr>
</tbody>
</table>

laboratory stage. When combined with a motorized stage, the control software of the instrument allows for coordinated sample stage movement and spectrum collection, so that, e.g., element distributions along a line on the specimen surface can be recorded.

The COPRA instrument is currently installed at the Academy of Fine Arts, Vienna, Austria. Other types of cultural heritage artefacts that were investigated with it include Medieval brass and bronze burial artefacts (Cu, Zn, Sn), early 20th century decorated glass objects (Mn, Fe, Co, Ni, Zn, Sn), daguerreotypes (Cu, Au, Ag), differently pigmented areas of 18th century illuminated parchments (Ca, Mn, Fe, Cu, Au, Pb) and various manuscripts from the 13th to the 19th centuries of the Austrian State Archives prepared with ferro-gallic ink, next to modern car paints [31], multi-coloured beads and industrial materials [84].

![Image](https://example.com/image.jpg) Fig. 4.45. Use of the COPRA instrument for in situ (i.e., in the museum gallery) analysis of a gold artefact.
For the chemical characterization of corrosion compounds analysis on ancient bronze objects, De Ryck et al. [85] have compared different micro-beam techniques. They include optical microscopy, SEM–EDX, secondary ion microscopy, synchrotron-based FTIR, synchrotron-based XRD and XANES. The objective was to investigate which combination of analysis methods is most suitable for this type of investigation, taking into account aspects such as limited sampling and the ability of obtaining spatial information. These authors state that XRD in combination with optical microscopy and SEM-EDX is able to provide a complete description of the layered structure both on the elemental and the molecular levels.

4.4.5 Analysis of graphic documents

Historical objects such as documents, illuminated manuscripts and coloured prints are not only valuable objects of cultural heritage but also documents of human history. The knowledge about historical materials is very important to answer archaeometrical questions and to develop and/or refine restoration and conservation concepts.

Historic inks contain, next to the constituents that are responsible for its colour (e.g., carbon/soot in bistre-type inks, Fe in ferro-gallic inks,…), impurities of various nature. Together, these non-essential components of the inks can form a characteristic fingerprint that can provide information on the manufacturing technology of the ink or that can be used to investigate additions, alternations and or falsifications made in different inks to historical documents.

Haller and Knöchel [36] and Mommsen [86] compared the concentrations of Cu and Pb in ink of the Gutenberg Bible to that of other early single leaf copies and books. The pioneering work with PIXE by Cahill et al. [87,88] identified the (X-ray based) analysis of ink as a new research tool for the history of early printing (from the second half of the 15th century) [89,90]. It is assumed that each printer/printing-office can be recognized by a specific ink-preparation as reflected in the trace element signature of the dried ink. The recipes for the ink were kept as a secret; in the 15th century, not a single specification of composition is documented [91].

Mommsen et al. [86] employed a $0.5 \times 1 \text{ mm}^2$ polychromatic X-ray beam derived from the synchrotron storage ring ELSA (Bonn, Germany) for irradiating single leaves of early 15th century printed paper. Ink and paper of 22 different works from different locations in Germany, Italy and Switzerland were analysed. The energy deposited in the paper during the
measurements (300 s) was estimated to be ca. 15 \( \mu \) W/cm\(^2\), i.e., about a factor 70 lower than bright sunlight.

Comparison of the spectra from paper and paper/ink combinations from page II,316 of the single leaf 42-line Gutenberg bible revealed that Ni, Cu and Pb are present in the ink at concentration levels of a few 10 \( \mu \)g/cm\(^2\) while K, Ca, Ti, Mn, Fe and Zn originate from the paper base.

In six of the 22 leaves, printed areas could not be distinguished from blank areas, suggesting that the corresponding inks were prepared from mainly C-bearing material such as lampblack or soot [91]. In some of the other inks, in addition to Ni, Cu and Pb, also K, Ca and Fe were present. On all analysed pages except the Gutenberg leaf, the same ink composition on the recto and verso side was found. On the recto side of the Gutenberg B-42 leaf, the ink thickness was ca. three times larger than on the verso side, although both sides show the same Cu/Pb and Ni/Pb ratios (respectively, 1.0 \( \pm \) 0.5 and 0.007 \( \pm \) 0.003). For the same page (II, 316) of the Harvard Gutenberg bible, by means of PIXE recto and verso Cu/Pb ratio’s of 1.15 \( \pm \) 0.05 and 1.44 \( \pm \) 0.07 were reported [86–89].

For three specific printers, the constancy of their ink composition over large time intervals was tested by analysing leaves of several books produced by them. They appear to have changed the composition of their inks fairly frequently. It therefore appears difficult to establish a definite trace element pattern specific for one printer. When only the trace elements which occur in the ink alone (and not in the paper) are considered, only Pb and Cu concentrations can be used for distinguishing between early printers.

As a result of this study, Mommsen et al. [86] concluded that a systematic investigation of the ink composition in works printed 10–15 years after Gutenberg’s first bible edition is needed to learn more about the early recipes for ink preparation and find specific reasons for the presence of metallic impurities in the ink. The synchrotron-based XRF method was found to be suitable for non-destructive measurements on this fragile type of material and appropriate for performing the large number of measurements required to reveal systematic trends in the composition of paper and inking.

Next to synchrotron-based XRF, laboratory \( \mu \)-XRF is also an excellent technique for the analysis of valuable documents, e.g., to determine their authenticity. Typically, different inks, while having the same visible appearance, will have different chemical compositions. Larsson [92] and Stocklassa and Nillson [93] described analysis by \( \mu \)-XRF of a 500-year-old Swedish possession letter (dated April 1, 1499). The document, a sales contract for an estate, showed signs of alterations. It was suspected that the alteration was made in the 1530s, when the Swedish king restituted land
back to certain nobles, who previously had been stripped of their estates by an earlier ruler. Although alteration was suspected by visual inspection (the original name of the owner had been removed by scraping), the original text was unreadable. By employing μ-XRF generated Ca and Zn maps (a trace constituent of the original ink), the original name could be established, however. In the Ca map, the (falsified) visible text was visible, featuring the family name “Gäsmestad i Böre”; in the Zn map of the same area, however, a completely different text reading “Bøtinge i Asbo” could be read. Obviously, the forger used different inks for the alteration, accounting for the change in chemical makeup.

In Fig. 4.46, the elemental ratios Mn/Fe, Cu/Fe and Zn/Fe obtained by means of μ-XRF investigations of Goethes manuscripts of Faust I and Faust II are intercompared. Folios GSA25/XVII,2,12; GSA25,XVII,1,2; (Faust I, original and corrections) and GSA25/XVIII,5,7 (Faust II) were examined by means of the ArtAX spectrometer at the Goethe und Schiller-Archiv (Weimar, Germany), yielding fingerprint spectra of the inks. It can be observed that the two inks employed by Goethe to write Faust I have a similar composition. The ink used for the corrections to Faust I are similar to the ink employed for writing Faust II, indicating that Goethe did not modify the first part until working on the second part (Fig. 4.47). These and other valuable manuscripts (e.g., music scores by Bach and Mozart) also have

![Fig. 4.46. Analysis results of J.W. von Goethes manuscripts of Faust I and II by means of the ARTAX μ-XRF spectrometer. The two inks used in Faust I (squares) show a similar composition; the ink used for corrections to Faust I (triangles) is similar to that used for Faust II (circles).]
been examined in the context of oxidative corrosion inflicted to the paper by ferro-gallic inks [94] (see also Chapter 17).

The ArtAX spectrometer was also used to investigate the pigments used for colouration of two similar copper engravings of Albrecht Dürer (Kupferstichkabinett, Berlin, Germany) entitled “Petrus und Johannes heilen einem Lahmen” (Peter and John healing a cripple). Both 16th century prints were coloured at a later time. XRF analysis revealed that one of the prints (KK Berlin Inv.-Nr. A137) was coloured with pigments such as azurite (blue), malachite (green), white lead, cinnabar (red), ochre (yellow-brown), red lead, gold water colour and crayon, consistent with a colouration made in

![Normalized absorption (a.u.)](image)

**Fig. 4.47.** Mn K-edge XANES spectra of: (a) fossilized ivory; (b) 600°C heated fossilized ivory; (c, d) turquoise-blue collection odontolites and (e) synthetic apatite Ba₅(PO₄)₂.₅(MnO₄)₀.₅Cl taken as reference mineral with Mn⁵⁺ in tetrahedral coordination. Inset: Pre-edge structure of tetrahedral Mn⁵⁺ in (b) heated fossilized ivory; (c, d) odontolites and (e) synthetic Ba₅(PO₄)₂.₅(MnO₄)₀.₅Cl are observed at 0.9 and 1.9 eV below those of tetrahedral Mn⁵⁺ in BaMnO₄ and Mn⁷⁺ in KMnO₄, respectively.
the 16th–17th century. In the second print (KK Berlin Inv.-Nr. A551), however, zinc oxide red and chromium green pigments were encountered, pointing to a colouration in the 19th century [95].

Silver point drawings belong to the most precious and rarest treasures of print collections. They were essentially created during the Renaissance and are characterized by extremely thin grey-brownish strokes on paper that had been coated before use. So far, only little chemical information on these drawing materials could be obtained because the drawings are very delicate, and, therefore, analyses are very difficult to perform without any damage. A chemical fingerprint can be obtained by the determination of ratios of selected elements, reflecting not only the origin of the used materials but also the processing and the storage conditions. In order to precisely characterize the chemical composition of drawings by Albrecht Dürer (1471–1528) and Jan van Eyck (ca. 1395–1441), Reiche et al. [96,97] employed synchrotron radiation-induced μ-XRF.

4.4.6 Mn oxidation in odontolites

In the Middle Ages, Cistercian monks created odontolite, a turquoise-blue gemstone, by heating fossilized mastodon ivory found in 13–16 million-year-old Miocene geological layers next to the Pyrenees. They thought they had produced the mineral turquoise because of the resemblance of odontolite with this semi-precious stone. Odontolite was used for the decoration of medieval art objects such as the reliquary bronze crosses. Fossilized ivory and its mysterious colour change upon heating have been investigated by several naturalists and gemmologists, among them Réaumur (1683–1757). Reiche et al. [98] investigated odontolite decorations on a 13th century cross, made in a Limoges workshop. Although vivianite, a blue-coloured iron phosphate or copper salts were proposed to be the colouring phases, none of these minerals were found in the odontolite material. Rather, it consisted of fluorapatite, Ca$_5$(PO$_4$)$_3$F, containing trace amounts of iron, manganese, barium, lead, rare earth elements and uranium and presenting crystallites of 100–500 nm in size. The crystal size was about 10 times larger than that of unheated fossilized ivory and suggested that odontolite was heated at about 600°C [99]. As potential colouring agents manganese and iron were then studied. Luminescence and optical spectroscopy permitted the exclusion of iron as a colouring ion and suggested that manganese ions could be responsible for the colouration of odontolite. XAS was employed to follow changes in the local environment and the valence state of manganese on heating. XANES and EXAFS spectra were recorded at the K-edge of
manganese impurities (200–650 ppm) in fluorapatite, which is a strongly absorbing matrix at this energy (6.5 keV). An energy resolution of 0.4 eV, realized by using the a Si(220) monochromator of ESRF Beamline ID26, was used to measure the position and the intensity of the pre-edge structure of manganese. They indicate most clearly the changes in the structural environment and oxidation state of manganese. Unheated (white) fossil ivory showed Mn$^{2+}$ ions in octahedral coordination while in the (turquoise-blue) fossilized ivory heated at 600°C and in the two odontolite samples, the major part of the manganese was found to be in the $5^+$ oxidation state as indicated by the pre-edge structure observed at 6541.3 eV. In addition, a comparison of the XANES spectra of heated fossilized ivory, odontolites and a reference synthetic Mn-chlorapatite indicated that the Mn$^{5+}$ substitutes for P$^{5+}$ at the tetrahedral sites; in such a coordination Mn$^{5+}$ ions give rise to an intense turquoise-blue colour.

On the basis of the XANES data, it could be concluded that the transformation of white mastodon ivory into turquoise-blue odontolite involves two phenomena: (1) a fossilization accompanied by an uptake of metal ions, specifically Mn ions (Mn$^{2+}$), possibly by sorption on apatite crystallites; and (2) a deliberate heating process in air above 600°C that oxidizes Mn$^{2+}$ into Mn$^{5+}$, which substitutes for P$^{5+}$ in the tetrahedral site of the apatite structure. This substitution occurs during the heat-induced crystal growth of apatite. Thus, the origin of the colour change in fossilized ivory during heating could clearly be demonstrated using XAS and, in contrast to former hypotheses, it could be shown that odontolite owes its turquoise-blue colour to traces of Mn$^{5+}$ ions in a distorted tetrahedral environment of four O$^{2-}$ ions.

4.4.7 Therapeutic and cosmetic chemicals of Ancient Egypt

The funerary furniture discovered in Egyptian tombs, dating from between 2000 BC and 1200 BC, provides lot of information about the customs of everyday life in Ancient Egypt [100]. Among these objects there was an abundance of toilet accessories: mirrors, hairpins, eyeliner applicators, combs or spatulas, and make-up receptacles, some of which are now preserved in the Egyptian Department of the Louvre Museum (Fig. 4.48).

Inside these three 4000-year-old containers made of marble, alabaster, wood or reed, cosmetic powders in an exceptionally good state of conservation were found. In order to obtain information on their composition and the methods used in their elaboration, the organic fractions of the cosmetics were analysed by chromatographic techniques and the mineral content by
scanning electron microscopy, FTIR spectrometry and powder XRD [101]. Conventional quantitative laboratory XRD was impeded by several factors: (a) owing to the high archaeological value of the powders, only small quantities could be extracted and analysed; (b) the as-found cosmetics are highly absorbing mixtures of lead-based compounds; (c) most mixtures contained as many as 10 phases, i.e., the resulting diffractograms display a complex series of overlapping Bragg lines. Measurements carried out at two synchrotron beamlines (ESRF BM16 and LURE DW22) were able to take advantage of the high flux, the high energy and the high resolution of the exciting radiation. The Rietveld refinement method was applied to determine the respective crystalline phase mass fractions. Taking into account the

Fig. 4.48. X-ray radiography of different makeup receptacles from the Egyptian collections of the Louvre Museum. The white areas show the distribution of the X-ray absorbing lead powders present in the make-up. (a) Reed case, still full of makeup; (b) alabaster recipient with a fabric lid; (c) alabaster recipient and cover. It contains a small amount of makeup attached on the inner wall.
anisotropic line profile of some phases, it was possible to significantly improve the fit agreement factors (to less than 10%) and detect quantities of minerals down to 0.5% (see Fig. 4.49).

Two natural compounds bound with some animal grease were identified: crushed ore of black galena (PbS) and cerussite (PbCO₃). Galena is still the basic constituent of many khols traditionally used in North Africa, Asia and the Middle-East nowadays. White cerussite was added to the composition in order to obtain a grey-to-white make-up. Rietveld analysis of the XRD patterns of the mixture revealed the presence of two more white constituents: laurionite (PbOHCl) and phosgenite (Pb₂Cl₂CO₃). These products are very rare in nature and could not have been extracted from the mines in sufficient quantities for the preparation of the cosmetics. These products could have been formed by chemical alteration and ageing, assuming the original content of the make-up receptacles had been in contact with carbonated and chlorinated waters. However, no clear trace and evidence of such alteration processes could be found in any of the 49 recipients.

Therefore one major conclusion of the work was that laurionite and phosgenite were intentionally manufactured by the Egyptians. The texts of Pliny the Elder and Dioscorides (1st century AD) report on a number of medical recipes. In particular some of them refer to the use of lead oxide that was ground and diluted into salted and sometimes carbonated...

Fig. 4.49. XRD pattern of a sample of Egyptian cosmetic powder (black curve) and Rietveld refinement. Open circles: calculated pattern on the basis of four components: black galena (PbS), cerussite (PbCO₃), phosgenite (Pb₂Cl₂CO₃) and laurionite (PbOHCl) (all white); grey curve: residual.
(natron) water. This wet process was mimicked in the laboratory. By maintaining the solution at a neutral pH, a slow reaction yields white precipitates of either laurionite or phosgenite. This is the first indication that wet chemistry has been practiced since 2000 BC.

The reason for adding the white lead derivatives PbOHCl and Pb₂Cl₂CO₃ to black PbS, instead of white cerussite (PbCO₃), is that since the earliest periods of Egyptian history, cosmetics were not only employed for aesthetic purposes, but also for their therapeutic and magic/religious properties. Greco-Roman texts mention, e.g., that white precipitates synthesized from PbO are appropriate for eye and skin care; these lead compounds could be used as a bactericide and as a protection for the eye against exposure to the sun’s rays.

The width of the diffraction peak profiles also permitted to compare the strain and crystallite size in archaeological, synthetic and natural powders [102,103]. XRD peak breadth analysis combined with SEM observations showed that the PbS ore present in the cosmetics was ground and sorted according to grain size. The resulting granulometry of galena provided the make-up with the expected texture and its metallic brightness. By contrast, the Bragg line broadening of PbOHCl and Pb₂Cl₂CO₃ is free from any strain: this suggests that they have been directly synthesized as fine powders and have not been prepared by crushing. In this manner, the XRD line broadening related to the crystallographic microstructure contributed to a better understanding of the origin and the process of elaboration of the archaeological powders.

The same authors also studied the effect of Pb-containing cosmetics on the structure and composition of ancient hair samples, obtained from different Egyptian mummies, by means of X-ray micro-beam techniques [104]. In native hair, the lipids are present as calcium soaps; μ-XRF and μ-XRD investigations performed at ESRF ID22 and ID13 showed that appropriate lead treatment considerably enhances the organized lipid features in hair [105]. The elemental micro-analysis of Egyptian mummy hair cross-sections, compared to native modern hair, showed a significant increase in content of specific trace elements. The observed elemental distribution across the hair sections differed noticeably between hairs originating from different mummies. XRF measurements of the hair of one of the mummies revealed a notable increase in calcium (146 μmol/g on average), zinc (37 μmol/g), iron (14 μmol/g) and lead (1.1 μmol/g) contents, compared to the maximum contents of these elements observed in native samples. Other trace constituents of native hair such as manganese (1.8 μmol/g), bromine (1.1 μmol/g), titanium (1.1 μmol/g) and strontium (0.62 μmol/g) also showed...
a significant increase. The elemental distribution across hair sections from a second mummy was found to be very heterogeneous (see Fig. 4.49). The localization of sulphur, mainly originating from hair proteins, enables a clear visualization of the hair section contour. Three types of elemental distribution could be distinguished:

(a) elements such as Ca that are similarly distributed in the fibber section as in current hair;
(b) elements concentrated specifically in some of the histological zones: Mn, Zn, Pb, Sr in the medullar canal and Fe, Cu and Pb in the peripheral areas of the hair strand;
(c) elements presents as impurities, deposited on the surface of the hair strand (Ti, Zn).

Considering that natron, the dehydration and purification agent used during mummification, is a complex mixture of sodium chlorides, sulphates, carbonates and bicarbonates, as well as containing small quantities of calcium carbonate, part of the trace element load in the hair must be assumed to originate from this treatment. Significant amounts of calcium and chlorine were observed in all samples while all trace elements associated with natron of the Greco-Roman period (Ca, Sr, Br, Cl, Fe, Mg) were found to be in excess in one of the examined hair samples. Apart from these elements, a very high content of Mn and Pb in the hair strands from both mummies was observed. These elements are particularly concentrated at the hair periphery and in the medulla of one of the samples. The presence of these elements was attributed to the use of Pb-based make-up and of Mn-based hair dyes in Ancient Egypt. The specific concentration of lead, calcium and other cations within the medullar canal, where the lipids were concentrated before mummification, could be related to the saponification of hair lipids. The absorption of exogenous metal cations within the fibber may have locally increased the electronic density of the material. The diffusion of metal ions can moreover have a structuring effect, by regularly organizing the keratins around the metal sites. This can be an explanation for the increase in contrast observed in the hair diffraction pattern (Fig. 4.50).

4.5 CONCLUSION

It can be concluded that X-ray techniques offer a variety of possibilities for non-destructively compositional and/or structural analysis of cultural heritage materials. Apart from determinations of the (local)
composition, which may be performed via XRF analysis, structural information on crystalline and amorphous phases can also be obtained via XRD and XAS. Next to standard laboratory equipment, which is not always suitable for analysis of large artefacts, open beam instrumentation is available, either under the form of compact transportable equipment for in situ measurements or as part of larger installations such as synchrotron facilities. Provenance analysis investigations as well as conservation studies can be executed in many cases by means of X-ray techniques.

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Fig. 4.50. X-ray fluorescence maps of a Mummy hair section. The hair diameter is ca. 150 μm. The elemental content (in μmol/g w/w) is indicated, followed by the ratio to average native hair trace element content.
APPENDIX A4.1 FIGURES-OF-MERIT FOR XRF SPECTROMETERS

A4.1.1 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 the outgoing fluorescent radiation in the material can be neglected, 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:

$$N_i = S_i m_i t = S_i c_i t$$  \hspace{1cm} (A4.1)

The proportionality constants $S_i$ for the various elements are called the sensitivity coefficients of the XRF spectrometer for determination of these elements (typically expressed in counts/s/(g/cm$^3$) or in counts/s/mg) and are important figures-of-merit of the instrument. 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 $R_i$:

$$R_i = N_i / t = S_i c_i$$  \hspace{1cm} (A4.2)

A4.1.2 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. The background intensity $B_i$ can be written as the sum of various contributions:

$$B_i = B_{i}^{\text{scatter}} + B_{i}^{\text{detector}} + \sum_{j \neq i} B_{i,j}^{\text{overlap}} + B_{i}^{\text{blank}}$$  \hspace{1cm} (A4.3)

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 artefacts, $B_{i,j}^{\text{overlap}}$ 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 \( \langle B_{i} \rangle \) 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 \( s_{B}^2 = \langle B_{i} \rangle \).

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 \( N_{i,LD} \) that can still be distinguished in a statistically significant
manner from the average background level can be written as:

\[
N_{i,LD} = \langle B_{i} \rangle + k s_{B}
\]  \hspace{1cm} (A4.4)

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:

\[
C_{i,LD} = \frac{N_{i,LD} - \langle B_{i} \rangle}{S_{i}t} = \frac{k s_{B}}{S_{i}t} = \frac{k \sqrt{R_{B}}}{S_{i} \sqrt{t}}
\]

where \( R_{B} = \langle B_{i} \rangle / t \) is the background count rate. When the irradiation of a
standard sample (with known concentration \( c_{j} \)) 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 \( N_{i}^{\text{std}} / c_{j}^{\text{std}} / t \), it follows that the lowest detectable
concentration (or relative detection limit) \( c_{i,LD} \) can be estimated from this
measurement by using the relation:

\[
c_{i,LD} \equiv c_{i}^{\text{std}} \frac{k \sqrt{B_{i}^{\text{std}}}}{N_{i}^{\text{std}}} \hspace{1cm} (A4.5)
\]

When during such an experiment, a known mass \( m_{i}^{\text{std}} \) was irradiated, the
lowest detectable mass (or absolute detection limit) \( m_{i,LD} \) can be calculated
X-ray based methods of analysis

by means of:

\[ m_{i,\text{LD}} \equiv m_{i}^\text{std} \frac{k \sqrt{B_{i}^\text{std}}}{N_{i}^\text{std}} \quad (A4.6) \]

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 \( \mu \)-XRF and 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 \textit{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.

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