

10.2.1.2 X-ray Generation

X-ray emission spectra characteristic of the analyte elements in a specimen may be excited by a variety of incident photons or accelerated particles. The two most frequently used types of excitation are by electrons (e.g., in electron microprobes or scanning electron microscopes) and by photons from X-ray tubes. However, other forms of excitation also exist. Terms related to X-ray generation are summarised in Table 10.2 together with their units and symbols.

10.2.1.2.1 X-ray generation by electrons

When a beam of electrons strikes a target or specimen, there are three ways in which the electrons may lose energy. Most electron interactions with atoms result in energy losses (a few eV) as heat generated in the material irradiated.

A small fraction, however, 1 part in 10^3 or less, of the electron interactions, ionize the atoms and may result in emission of a characteristic photon (see 10.2.1.2.3). The *cross section for ionization* by electrons, Q , describes the probability of such an ionization. Its customary unit is cm^2 and is usually given as the cross section for producing a particular kind of ionization, e.g., Q_K , Q_{LII} , etc., where the subscript refers to the shell or subshell ionized. Q is used in the equation $dA/dx = qQ_i n_i$, where q is the number of electrons per cm^2 incident normal to the thin layer of material containing n_i atoms per unit volume of element i and producing dA ionizations in a layer of thickness dx and area 1 cm^2 . As will be shown later (section 10.2.1.2.6.), Q is closely related conceptually and mathematically to the photoelectric absorption coefficient for radiation. The value of Q is relatively constant for all electron energies greater than about two times the binding energy of the shell. Thus, it is the increased path length for high energy electrons which increases the yield (X-ray photons produced per incident electron) rather than a change in ionization cross section.

Some of the incident electrons (the order of 1 part in 10^3) undergo interactions in which they lose hundreds of thousands of electron volts of energy by deceleration, but do not ionize the atoms. These interactions do generate X-ray photons, however, and the photons emitted in these instances form a spectral continuum. The spectral distribution rises sharply from the *Duane-Hunt short wavelength limit*, λ_{min} (corresponding to the maximum incident electron energy), reaches a peak at between 1.5 and 2 times the minimum wavelength, λ_{min} and decreases slowly at longer wavelengths. This continuum spectrum is often called *Bremsstrahlung* and appears as an interfering background in the measurement of characteristic lines.

In the case of the continuum spectrum, it is appropriate to speak of *spectral intensity*, I . (Note: use of the term I_θ meaning intensity measured as a function of angle is discouraged because its value is dependent on the inter-planar spacing of the crystal used.) Subscripts λ or E maybe added depending on whether the measurement is in units

of wavelength or energy (for practical units see Table 10.2). The measured value must be corrected for detector efficiency and crystal reflectance.

10.2.1.2.2 X-ray generation by positive ions

Ions are similar to electrons in the way they generate X-rays, except they do not generate a measurable continuum directly. However, the electrons they eject from the atoms do generate a spectral continuum.

10.2.1.2.3 X-ray generation by photons

The most common means of exciting characteristic X-ray photons for spectrochemical analysis is by use of photon radiation from an X-ray tube to ionize the sample atoms. The photon-excitation followed by photon emission is called *X-ray fluorescence*. Radiation from the X-ray tube is called the *primary radiation*; fluorescent X-rays are called *secondary radiation*. Primary radiation is generally plotted in terms of spectral intensity, I_λ or I_E , or tabulated as $I_\lambda\Delta\lambda$ or $I_E\Delta E$; the tables list the number of photons in a specified $\Delta\lambda$ or ΔE interval. For a primary photon to excite characteristic emission, its energy must exceed the binding energy or ionization energy of electrons in one of the electron shells. The binding energy is designated as $E_{K\text{ abs}}$, $E_{L\text{I abs}}$, etc. The corresponding wavelength is called the characteristic *absorption edge wavelength* and is given by $\lambda_{K\text{ abs}}$, etc.

10.2.1.2.4 Terms related to X-ray measurements

Characteristic X-rays from the different elements are distinguished either by their wavelength, λ , or by their energy, E , depending on the type of measuring equipment employed. Two important parameters control the characteristic X-ray intensity emitted by each element in a specimen, the *photon emission yield (fluorescence yield)* and the *linear attenuation coefficient*, μ .

10.2.1.2.5 Photon emission yield (fluorescence yield), ω

When the outer-shell electron fills the inner-shell vacancy in an ionized atom, a characteristic photon or another outer shell electron will be emitted (such an emitted electron is called an Auger electron). The fluorescence yield is the probability that the emission will be a photon. The fluorescence yield is less than 10% for low atomic-number elements, but approaches unity for high atomic number elements. According to the shell originally ionized, the fluorescent yield is designated ω_K , $\omega_{L\text{I}}$, etc.

10.2.1.2.6 Linear attenuation coefficient, μ

When a beam of X-rays passes through material, the reduction in intensity per unit distance travelled is represented by the linear attenuation coefficient. The attenuation is made up of two components: τ , the *linear photoelectric absorption coefficient*, and σ , the *linear scattering coefficient*. For the wavelengths commonly employed in analysis (from elements $Z > 10$), τ is usually more than 10 times greater than σ . Ionization of atoms is related only to the τ component and can be expressed as $dA/dx = -dq/dx = \tau q$, where q represents the number of photons lost by photoelectric absorption per unit distance travelled. The ratio of the absorption coefficients on the two sides of an absorption edge is the *absorption edge jump ratio*, r .

10.2.1.2.7 Mass attenuation coefficient, μ/ρ

When treating X-ray transmission in multiple-component samples, it is customary to use the *mass attenuation coefficients*, μ/ρ rather than the linear attenuation coefficient, μ , where ρ is the density. For convenience, the mass attenuation coefficient of matrix element j for the characteristic radiation of analyte element i , is frequently written as μ_{ij} . For a k component matrix M (including analyte element i), the total mass attenuation coefficient μ_{ik} is simply

$$\mu_{ik} = \sum_{j=1}^k \mu_{ij} c_j \quad (2)$$

where c_1, c_2 , etc. are the concentration of the elements expressed as fractions.

TABLE 10.2 Terms related to X-ray generation

Name	Practical Units	Symbol
X-ray intensity	s^{-1}	I
Relative X-ray intensity	1	I_r
Spectral intensity	$s^{-1} \text{ \AA}^{-1}$	I_λ
	$s^{-1} \text{ eV}^{-1}$	I_E
Ionization energy; Binding energy, for shell indicated	J...eV, keV	$E_i; E_K, E_{L II}, E_M$, etc
Energy of emitted photon	J...eV, keV	$E_{K\alpha}, E_{L\beta}$, etc
Absorption edge wavelength	nm, \AA	$\lambda_i, \lambda_{K \text{ abs}}, \lambda_{L \text{ abs}}$, etc
Wavelength of emitted photon	nm, \AA	$\lambda_{K\alpha}, \lambda_{K\beta}, \lambda_{L\alpha}$, etc
Absorption edge jump ratio	1	r
Cross section for ionization by electrons; for a specific electron shell	cm^2	$Q; Q_K, Q_{L II}$, etc
Linear attenuation coefficient for photons	cm^{-1}	μ
Mass attenuation coefficient for photons	$\text{cm}^2 \text{ g}^{-1}$	$\mu/\rho, \mu_{ij}, \mu_i$
Linear photoelectric absorption coefficient	cm^{-1}	τ
Linear scattering coefficient	cm^{-1}	σ
Photon emission yield (fluorescence yield); for a specific shell	1	$\omega, \omega_K, \omega_{L III}$, etc

10.2.1.2.8 Secondary fluorescence

Secondary fluorescence refers to ionization of the analyte element in a sample by characteristic radiation from other elements in the sample resulting in enhancement of the signal measured. *Secondary fluorescence* often makes an important contribution for elements $Z \geq 20$.