

X-Ray Spectroscopy*

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8.1 ORIGIN OF X-RAY SPECTRA

X-rays were discovered in 1895 by Wilhelm Conrad Röntgen who received the first Nobel Prize in Physics, awarded in 1901, for his discovery. X-ray absorption, emission, and fluorescence spectra are used in the qualitative and quantitative determination of elements in solid and liquid samples. XRA is used in the nondestructive evaluation of flaws in objects, including voids or internal cracks in metals, cavities in teeth, and broken bones in humans, a technique called radiography or X-ray fluoroscopy. This same technique is used to perform security screening of baggage at airports. A computerized version of radiography, computed tomography (CT) scanning or computed axial tomography (CAT), provides a powerful, high-resolution medical diagnostic tool by giving a 3D cross-sectional image of body tissues. Diffraction of X-rays by crystalline materials, a technique called X-ray crystallography, provides crystal structure identification, orientation of atomic planes in materials, and other physical information about samples. X-ray astronomy uses cosmic X-rays to study the universe, and X-ray spectrometers have been sent to the moon and Mars to study the surface rocks in situ. This chapter will focus primarily on X-ray fluorescence (XRF) spectrometry and X-ray diffractometry (XRD), the techniques of most use to analytical chemists. *X-rays:*

X-rays consist of electromagnetic radiation with a wavelength range from 0.005 to 10 nm (0.05–100 Å). X-rays have shorter wavelengths and higher energy than ultraviolet (UV) radiation. X-rays are generated in several ways, by deceleration of electrons in matter or by electronic transitions of inner core electrons.

8.1.1 Energy Levels in Atoms

Atom, shells, electrons:
An atom is composed of a nucleus and electrons. The electrons are arranged in shells around the nucleus with the valence electrons in the outer shell. The different shells correspond to the different principal quantum numbers of the possible quantum states. The principal quantum number, n , can have integral values beginning with 1. The shells are named starting with the shell closest to the nucleus, which is called the K shell. The K shell is the lowest in energy and corresponds to the quantum level with $n = 1$. The shells moving out from the nucleus are named the L shell, M shell, and so on alphabetically. The letters used for the two lowest shells are historical; K is from the German word *kurz*, meaning short, and L is from the German word *lang*, meaning long. An atom is shown

* Dedicated to the memory of Dr. Ron Jenkins and Dr. Eugene Bertin, outstanding X-ray spectroscopists and excellent teachers.

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x-ray production:

schematically in Figure 8.1a, with Φ_K , Φ_L , and Φ_M representing the energy of the K, L, and M shells, respectively. A partial list of elements and their electron configurations is given in Table 8.1. For example, a sodium atom contains filled K and L shells and one electron in the M shell.

When an X-ray photon or a fast-moving electron collides with an atom, its energy may be absorbed by the atom. If the X-ray photon or electron has sufficient energy, it knocks an electron out of one of the atom's inner shells (e.g., the K shell), and the atom becomes ionized as shown in Figure 8.1b. An electron from a higher-energy shell (e.g., the L shell) then falls into the position vacated by the dislodged inner electron, and an X-ray photon is emitted as the electron drops from one energy level to the other (Figure 8.1c). The wavelength/energy of this emitted X-ray photon is characteristic of the element being bombarded. *Auger e⁻ Spectroscopy:*

A fourth process can also occur, as shown in Figure 8.1d. Instead of emitting an X-ray photon, the energy released knocks an electron out of the M shell. This electron is called an Auger electron. This Auger process is the basis for a sensitive surface analysis technique. Auger electron spectroscopy (AES) and the related method of X-ray photoelectron spectroscopy, based on the measurement of the emitted electron shown in Figure 8.1b, are discussed in Chapter 14.

If we plot the energy levels of the K, L, and M shells for a given element, we get a diagram similar to Figure 8.2. *Energy levels:*

Note that the K shell has only one energy level, while the higher shells have sublevels within each shell. If an electron is dislodged from the K shell, an electron from an L or an M shell may replace it. The resulting ion emits radiation with energy E equal to the energy difference between the electronic energy levels, such as

$$E_{X\text{-ray}} = \Phi_L - \Phi_K \quad (8.1)$$

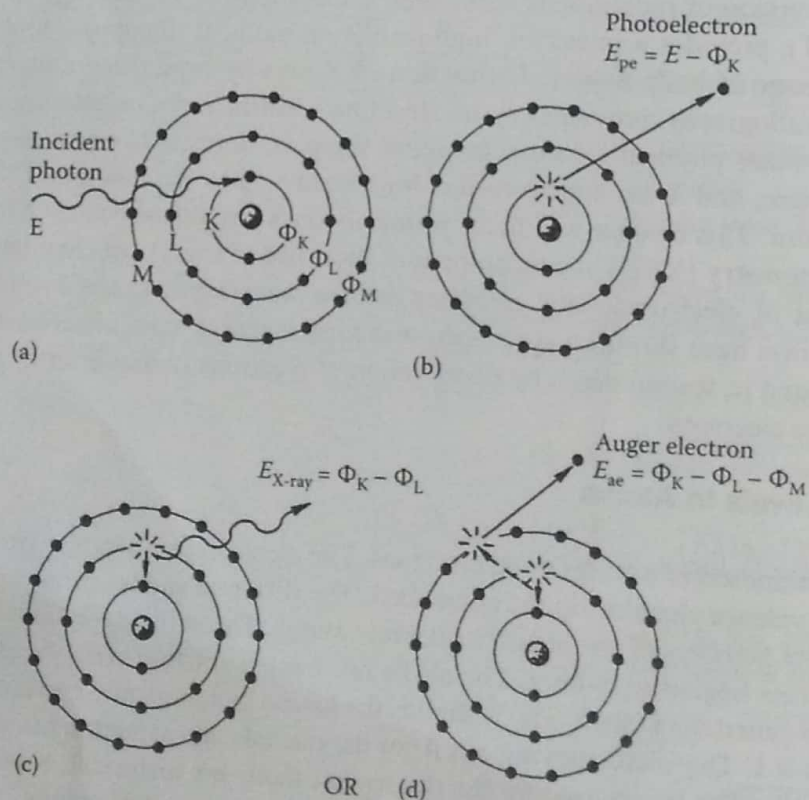


Figure 8.1 A schematic atom showing the steps leading to the emission of an X-ray photon (c) or an Auger electron (d). (From Jenkins, R. et al., *Quantitative X-Ray Spectrometry*, Marcel Dekker, Inc., New York, 1981. With permission.)

Table 8.1 Electron Configurations of Various Elements

Element	Z	K		L			M			N	
		1s	2s	2p	3s	3p	3d	4s	4p		
H	1	1									
He	2	2									
Li	3	2	1								
Be	4	2	2								
B	5	2	2	1							
C	6	2	2	2							
N	7	2	2	3							
O	8	2	2	4							
F	9	2	2	5							
Ne	10	2	2	6							
Na	11	Neon core (10)			1						
Mg	12				2						
Al	13				2	1					
Si	14				2	2					
P	15				2	3					
S	16				2	4					
Cl	17				2	5					
Ar	18				2	6					
K	19	Argon core (18)								1	
Ca	20									2	
Sc	21							1		2	
Ti	22							2		2	
V	23							3		2	
Cr	24							5		1	
Mn	25							5		2	
Fe	26							6		2	
Co	27							7		2	
Ni	28							8		2	
Cu	29							10		1	
Zn	30	Cu ⁺ core (28)								2	
Ga	31									2	1
Ge	32									2	2
As	33									2	3
Se	34									2	4
Br	35									2	5
Kr	36									2	6

where Φ_L is the energy of the electron in a specific electronic state within the L shell that "drops" to the K shell. Similar equations may be written for other transitions, such as between an M shell sublevel and an L shell sublevel, using the appropriate energy of the electron in the M shell sublevel that drops into the L shell and so on. As we know from Chapter 2,

$$E = h\nu = \frac{hc}{\lambda}$$

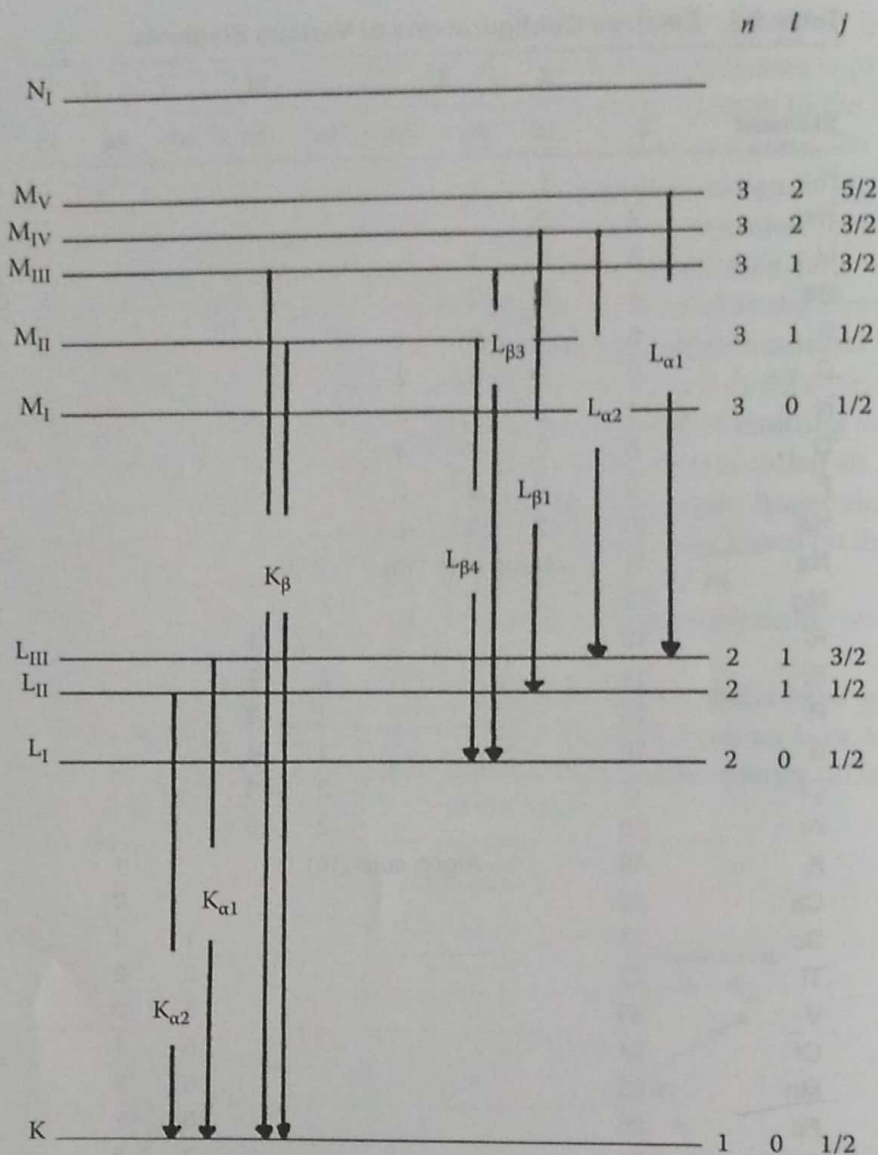


Figure 8.2 Atomic energy levels and symbols used for some common X-ray transitions. (Modified from Parsons, M.L., X-ray methods, in Ewing, G.W. (ed.), *Analytical Instrumentation Handbook*, 2nd edn., Marcel Dekker, Inc., New York, 1997. Used with permission.)

This relationship relates the energy of the emission to the wavelength and can be used to convert wavelength and energy. Most X-ray systems express wavelength in angstroms and energy in keV. To convert between these units, Equation 8.2 gives

$$\text{Energy (keV)} = \frac{12.4}{\lambda} (\text{\AA}) \tag{8.2}$$

Therefore, for the X-ray photon released when an L electron in a specific sublevel drops down to fill a vacancy in the K shell,

$$h\nu = \frac{hc}{\lambda} = \Phi_L - \Phi_K$$

Hence the frequency of the emitted X-ray is

$$\nu = \frac{\Phi_L - \Phi_K}{h} \tag{8.3}$$

The frequency or wavelength for transitions between other sublevels and shells is calculated in the same manner. Transitions are not possible between all available energy levels.

As in all forms of spectroscopy, transitions are governed by quantum mechanical *selection rules*. Some transitions are allowed by these rules while others are forbidden. For a brief discussion of the selection rules, the interested student should consult the texts by Jenkins or Bertin listed in the bibliography. *Emission lines:*

X-ray emission lines from electron transitions terminating in the K shell are called K lines, lines from transitions terminating in the L shell are called L lines, and so on. There are three L levels differing by a small amount of energy and five M levels. These sublevels are different quantum states, as shown in Figure 8.2; the quantum numbers and states will not be discussed here in detail. An electron that drops from an L shell sublevel to the K shell emits a photon with the energy difference between these quantum states. This transition results in a K_α line. There are two possible K_α lines for atoms with atomic number >9: K_{α1} and K_{α2}, which originate in different sublevels of the L shell. The K_α lines are often not resolved, and only one peak is seen. These lines are illustrated in Figure 8.2. The use of a Greek letter and numerical subscript to identify an X-ray emission line is called the Siegbahn notation. For the purposes of this text, the notation is just a "name" for the peak. An electron that drops from an M shell sublevel to the K shell generates a K_β X-ray. There is more than one K_β line, but the energy differences are so small between K_{β1} and K_{β2} that only a single K_β line is seen unless a high-resolution spectrometer is used. If an electron is ejected from an L shell, an electron from an M shell may fall into its place and emit an X-ray of characteristic wavelength with energy equivalent to the difference between the L and M shell sublevels. These are designated as L lines. A number of L lines are possible, as indicated by Figure 8.2. Table 8.2 indicates the actual transition that gives rise to selected X-ray emission lines. Electrons originating in an N or O shell and falling into the L shell also generate L lines. The energy levels of the K, L, M, and higher shells are characteristic of the element being examined, and the sharp emission lines resulting from electronic transitions are called characteristic lines or characteristic radiation. A schematic X-ray emission spectrum obtained under certain conditions by bombarding a solid metal, such as rhodium or lead or silver, with high-energy electrons is shown in Figure 8.3. The characteristic lines are shown as sharp peaks on a broad continuous background. The characteristic K and L lines for some elements are given in Table 8.3. A more comprehensive table of K and L lines for the elements is found in Appendix 8.A and in handbooks such as the *CRC Handbook of Chemistry and Physics* and the *CRC Handbook of Spectroscopy*, Vol. 1. Not all X-ray lines have a Siegbahn designation, so the International Union of Pure and Applied Chemistry (IUPAC) established

Table 8.2 Electron Transitions for Selected X-Ray Emission Lines

Siegbahn Line Designation	Electron Transition	Siegbahn Line Designation	Electron Transition
K _{α1}	L _{III} → K	L _{β1}	M _{IV} → L _{II}
K _{α2}	L _{II} → K	L _{β2}	M _{III} → L _I
K _{β1}	M _{III} → K	L _{β3}	M _{II} → L _I
K _{β2}	M _{II} → K	L _γ	M _I → L _{II}
K _{β3}	M _{IV, V} → K	L _{γ2,3}	N _{II, III} → L _I
K _{β4}	N _{II, III} → K	L _{γ6}	N _I → L _{III}
K _{β5}	N _{IV, V} → K	M _{ε1}	N _{III} → M _V
L _{α1}	M _V → L _{III}	M _{ε2}	N _{II} → M _{IV}
L _{α2}	M _{IV} → L _{III}		

Note: Not all lines are seen for all elements, and many of the lines are not resolved with standard X-ray spectrometers. Many M → M, N → M, O → L, and O → M transitions have no Siegbahn notation associated with them.

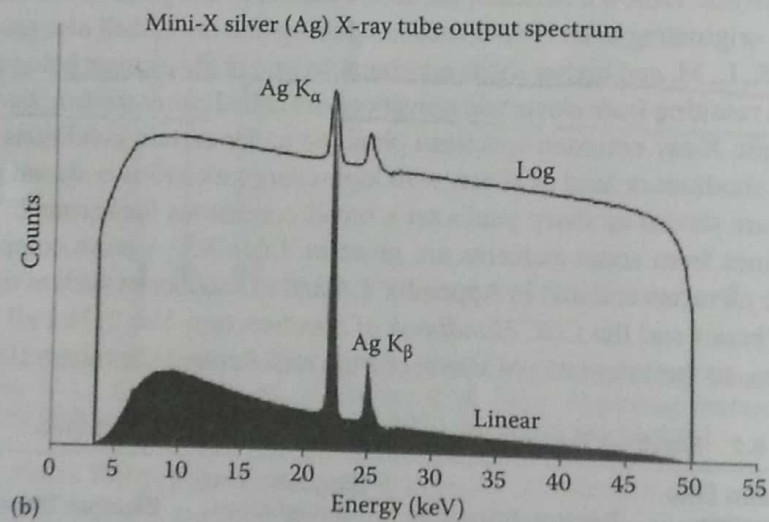
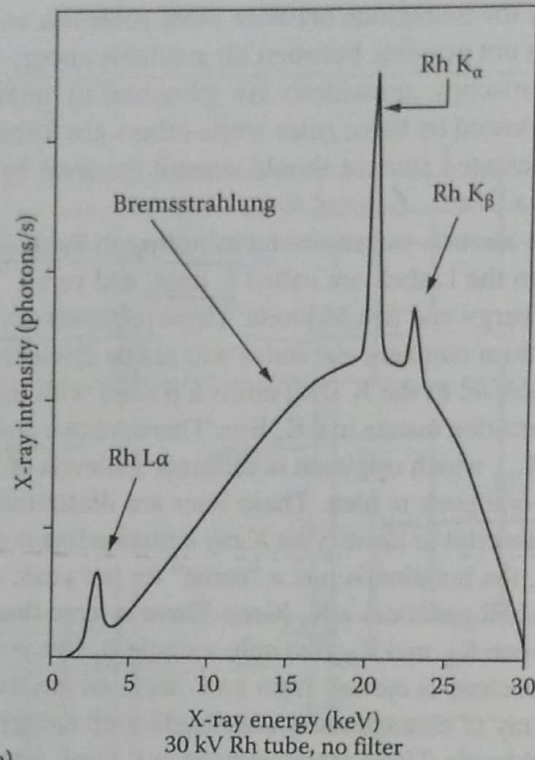


Figure 8.3 X-ray emission spectrum obtained by bombarding (a) rhodium metal (Rh) and (b) silver metal (Ag) with electrons. Both a broad continuum (Bremsstrahlung) and sharp characteristic emission lines from the metal are seen. (a: © Thermo Fisher Scientific. www.thermofisher.com. Used with permission; b: Amptek Mini-X silver (Ag) XRF tube output spectrum; Courtesy of Amptek, Inc., Bedford, MA, www.amptek.com.)

a new identification system for X-ray lines in 1991. Appendix 8.A contains a list of the Siegbahn notation for lines and the IUPAC designation for these lines. For all new publication purposes, the IUPAC designation should be used. *significance:*

The wavelengths and energies of the characteristic lines depend only on the element, because the inner electrons do not take part in bonding. Therefore, the lines are independent of oxidation state and bonding and physical state, making the use of the characteristic lines an elemental analysis technique. No molecular information is obtained from these lines.

Table 8.3 Wavelengths of Absorption Edges and Characteristic Emission Lines of Various Elements

Element	K Absorption Edge (Å)	Emission (Å)	
		$K_{\beta_{1,3}}$ ^a	$K_{\alpha_{1,2}}$ ^b
Mg	9.512	9.559	9.890
Ti	2.497	2.514	2.748, 2.752
Cr	2.070	2.085	2.290, 2.294
Mn	1.896	1.910	2.102, 2.106
Ni	1.488	1.500	1.658, 1.662
Ag	0.4858	0.4971, 0.4977	0.5594, 0.5638
Pt	0.1582	0.1637, 0.1645	0.1855, 0.1904
Hg	0.1492	0.1545, 0.1553	0.1751, 0.1799

^a When more than one number is listed, K_{β_1} is listed first.

^b When more than one number is listed, K_{α_1} is listed first.

Bremsstrahlung / white radiation:

The broad continuous "background" emission of x-radiation seen in Figure 8.3 is due to a second process that occurs when high-energy electrons strike a solid. The continuous radiation results from the collision of electrons with the atoms of the solid. At each collision, the electron loses some energy and decelerates, with the production of an X-ray photon. The energy of the photon is equal to the kinetic energy difference of the electron as a result of the collision. Each electron generally undergoes a series of collisions with each collision resulting in a photon of slightly different energy. The result of these many collisions is emission of a continuum of X-rays over a wide wavelength range. This continuous radiation is called *Bremsstrahlung* or *white radiation*.

When all the energy of the impinging electrons is turned into X-rays, as would occur if the electrons transferred all their energy in one collision, the wavelength of the emitted photons is the shortest attainable. This is termed the minimum λ or λ_{\min} . The radiation with the highest energy (and therefore the shortest wavelength) is deduced as follows. When all the energy of the electrons is converted to radiant energy, then the energy of the electrons equals the energy of the radiation. The energy of the radiation is given by $E = h\nu$, whereas the energy of the electrons is given by $E = eV$. When they are equal, $h\nu = eV$, where e is the charge of the electron; V , the applied voltage; and ν , the frequency of the radiation. But

$$\nu = \frac{c}{\lambda}$$

where

c is the speed of light

λ is the wavelength of radiation

Therefore,

$$h\nu = \frac{hc}{\lambda} = eV \quad (8.4)$$

Rearranging, we get

$$\lambda = \frac{hc}{eV} \quad (8.5)$$

When all the energy of the electron is converted to x-radiation, the wavelength of the radiation is a minimum, and we achieve minimum λ conditions:

$$\lambda_{\min} = \frac{hc}{eV} \quad (8.6)$$

Inserting the values for h , c , and e , which are constants, we have the **Duane-Hunt law**,

$$\lambda_{\min} = \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m/s})(10^{10} \text{ \AA/m})}{(1.60 \times 10^{-19} \text{ C}) \times V} = \frac{12,400}{V} \quad (8.7)$$

where

h is Planck's constant

c is the speed of light

e is the charge of an electron

V is the applied voltage (in volts)

λ_{\min} is the shortest wavelength of X-rays radiated (in angstroms)

The continuum radiation spectrum from a solid metal therefore has a well-defined short-wavelength limit. This limit is a function of the accelerating voltage, but not of the solid metal. The same λ_{\min} would be obtained by bombardment of lead or tungsten or rhodium at the same accelerating voltage. *x-ray emission spectrum:*

An X-ray emission spectrum is similar for all elements, in that K_{α} , K_{β} , and L_{β} lines may be seen, if the element possesses enough electrons to populate the appropriate levels. However, the actual wavelengths of these lines vary from one element to another, depending on the atomic number of the particular element. A mathematical relationship was discovered between the wavelengths of the K series and the atomic number of the element, and similar relationships were found for the L lines, and others.

8.1.2 Moseley's Law

Henry Moseley, a young graduate student working at Cambridge, UK, in 1913, discovered the relationship between wavelength for characteristic X-ray lines and atomic number. After recording the X-ray spectra from numerous elements in the periodic table, he deduced the mathematical relationship between the atomic number of the element and the wavelength of the K_{α} line. A similar relationship was found between the atomic number and the K_{β} line, the L_{α} line, and so on. The relationships were formulated in Moseley's law, which states that

$$\nu = \frac{c}{\lambda} = a(Z - \sigma)^2 \quad (8.8)$$

where

c is the speed of light

λ is the wavelength of the X-ray

a is the constant for a particular series of lines (e.g., K_{α} or L_{α} lines)

Z is the atomic number of the element

σ is the screening constant that accounts for the repulsion of other electrons in the atom

A partial Moseley's law plot for the K_{α} , K_{β} , L_{α} , and L_{β} emission lines is shown in Figure 8.4. Shortly after this monumental discovery, Moseley was killed in action in World War I. The impact of Moseley's law on chemistry was substantial, in that it provided a method of unequivocally assigning an atomic number to newly discovered elements, of which there were several at that time. In addition, it clarified disputes concerning the positions of all known elements in the periodic table, some of which were still in doubt in the early part of the twentieth century.

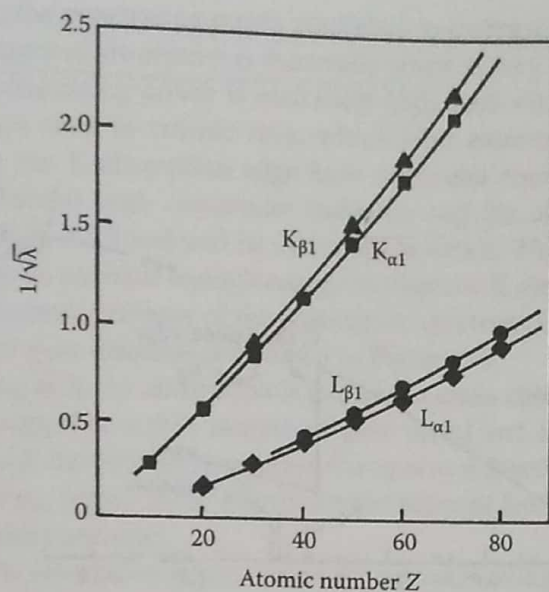


Figure 8.4 Partial Moseley's law plots for selected K and L lines, showing the relationship between the X-ray emission wavelength and atomic number of the element. Using this relationship, it was possible to predict undiscovered elements and to correctly assign atomic numbers to known elements. (From Helsen, L.A. and Kuczumow, A., in Van Griekin, R.E.; Markowicz, A.A. (eds.), *Handbook of X-Ray Spectrometry*, 2nd edn. Marcel Dekker, Inc.: New York, 2002. Used with permission.)

8.1.3 X-Ray Methods

There are several distinct fields of X-ray analysis used in analytical chemistry and materials characterization, namely, XRA, XRD, XRF, and X-ray emission. The basic principles of each are described in the following. X-ray emission is generally used for microanalysis, with either an electron microprobe (Chapter 14) or a scanning electron microscope (SEM).

8.1.3.1 X-Ray Absorption Process

The absorption spectrum obtained when a beam of X-rays is passed through a thin sample of a pure metal is depicted in Figure 8.5.

As is the case with other forms of radiation, some of the intensity of the incident beam may be absorbed by the sample while the remainder is transmitted. We can write a Beer's law expression for the absorption of X-rays by a thin sample:

$$I(\lambda) = I_0(\lambda)e^{-(\mu_m)\rho x} \quad (8.9)$$

where

$I(\lambda)$ is the transmitted intensity at wavelength λ

$I_0(\lambda)$ is the incident intensity at the same wavelength

μ_m is the **mass absorption coefficient** (cm^2/g)

ρ is the density of the sample (g/cm^3)

x is the sample thickness (cm)

The mass absorption coefficient is a constant for a given element at a given wavelength and is independent of both the chemical and physical state of the element. An updated compilation of mass absorption coefficients can be found online at the NIST website: <http://www.nist.gov/pml/data/xraycoef/index.cfm> (J.H. Hubbell and S.M. Seltzer) or in the text by Bertin or handbooks listed in the bibliography or references in the literature.

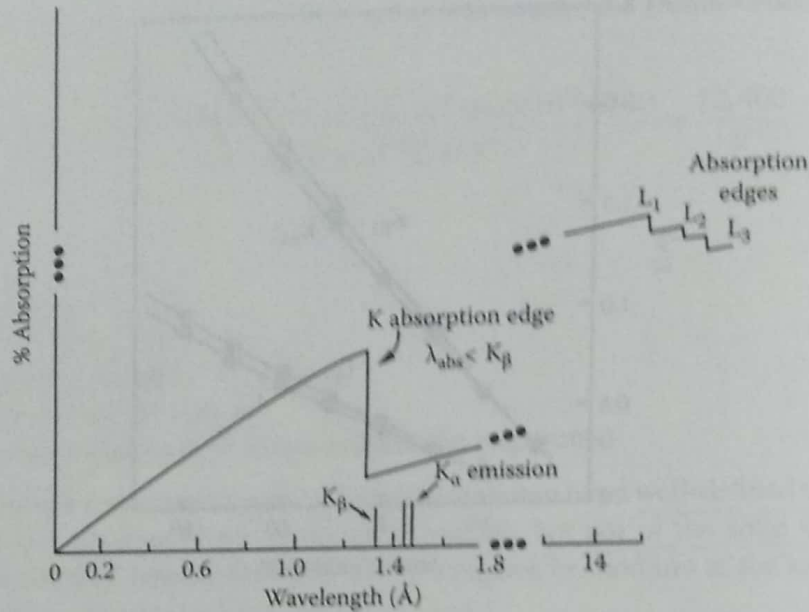


Figure 8.5 The X-ray absorption spectrum of a pure metal. Longer wavelengths are more readily absorbed than shorter wavelengths. The absorption spectrum is characterized by absorption edges, which are abrupt increases in absorption at energies sufficient to eject an electron from one of the atomic shells. The K absorption edge occurs at an energy sufficient to eject an electron from the K shell of the given metal.

Of course, most samples do not consist of a single pure element. The total mass absorption coefficient for a sample can be calculated by adding the product of the individual mass absorption coefficients for each element times the weight fraction of the element present in the sample. That is, for a metal alloy like steel,

$$\mu_{\text{total}} = w_{\text{Fe}}\mu_{\text{Fe}} + w_{\text{Cr}}\mu_{\text{Cr}} + w_{\text{Ni}}\mu_{\text{Ni}} + \dots \quad (8.10)$$

where

w_{Fe} is the weight fraction of iron

μ_{Fe} is the mass absorption coefficient for pure iron

w_{Cr} is the weight fraction of chromium, and so on for all the elements in the alloy

For accurate quantitative work, the *mass attenuation coefficient* is used in place of the mass absorption coefficient. The *mass attenuation coefficient* takes into account both absorption and scattering of X-rays by the sample. $\% A \propto \lambda \propto \frac{1}{E} \propto \downarrow \text{penetrating power}$

The amount of light absorbed increases as the wavelength increases. This is reasonable since longer wavelengths have less energy, and a less energetic photon has less "penetrating power" and is more likely to be absorbed. Only a few absorption peaks are seen in an X-ray absorption spectrum, but there is a very distinct feature in these spectra. An abrupt change in absorptivity (or the mass absorption coefficient) occurs at the wavelength of the X-ray necessary to eject an electron from an atom. These abrupt changes in X-ray absorptivity are termed *absorption edges*. Looking at Figure 8.5, it can be seen that radiation with a wavelength of 1.8 Å has a certain percent absorption value. As the wavelength of the X-ray decreases, its energy increases, its penetrating power increases, and the percent absorption decreases. This can be seen by the downward slope of the absorption trace, moving to the left along the x-axis from a wavelength of 1.8 Å. As the wavelength decreases further, the X-ray eventually has sufficient energy to displace electrons from the K shell. This results in an abrupt increase in absorption. This is manifested by the **K absorption edge**.