

Figure 8.3 X-ray emission spectrum obtained by bombarding rhodium metal (Rh) with electrons. Both a broad continuum (bremsstrahlung) and sharp emission lines from rhodium are seen. [Courtesy of ThermoNoran (www.thermo.com)]

of Spectroscopy, Vol. 1. Not all X-ray lines have a Siegbahn designation, so the IUPAC established a new identification system for X-ray lines in 1991. Appendix 8.1 contains a list of the Siegbahn notation for lines and the IUPAC designation for these lines.

The wavelengths 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, bonding, and physical state, making the use of the characteristic lines an *elemental* analysis technique. No molecular information is obtained from these lines.

The broad continuous “background” emission of X-radiation seen in Fig. 8.3 is due to a second process that occurs when high-energy electrons strike a solid metal. The continuous radiation results from the collision of electrons with the atoms of the solid. At each

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

Element	K absorption edge (\AA)	Emission (\AA)	
		$K_{\beta 1,2}$ ^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

^aWhen more than one number is listed, $K_{\beta 1}$ is listed first.

^bWhen more than one number is listed, $K_{\alpha 1}$ is listed first.

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 and λ is the wavelength of radiation. Therefore,

$$h\nu = \frac{hc}{\lambda} = eV \quad (8.3)$$

Rearranging, we get

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

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:

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

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

$$\lambda_{\min} = \frac{(6.626 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ m/s})(10^{10} \text{ \AA/m})}{(1.60 \times 10^{-19} \text{ C}) \times V} = \frac{12,400}{V} \quad (8.6)$$

where h is Planck's constant; c , the speed of light; e , the charge of an electron; V , the applied voltage (in volts); and λ_{\min} , 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.

The Duane–Hunt Law gives the conversion factor between energy and wavelength. Most X-ray systems express wavelength in angstroms and energy in keV. To convert between these units, Eq. (8.6) gives:

$$\text{Energy (keV)} = \frac{12.4}{\lambda(\text{\AA})} \quad (8.7)$$

An X-ray emission spectrum is similar for all elements, in that K_{α} , K_{β} , L_{α} , 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

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

where c is the speed of light; λ , the wavelength of the X-ray; a , a constant for a particular series of lines (e.g., K_{α} or L_{α} lines); Z , the atomic number of the element; and σ , a 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 Fig. 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 20th century.

8.1.3. X-Ray Methods

There are several distinct fields of X-ray analysis used in analytical chemistry and materials characterization; namely, X-ray absorption, X-ray diffraction, X-ray fluorescence, and X-ray emission. X-ray emission is generally used for microanalysis, with either an electron

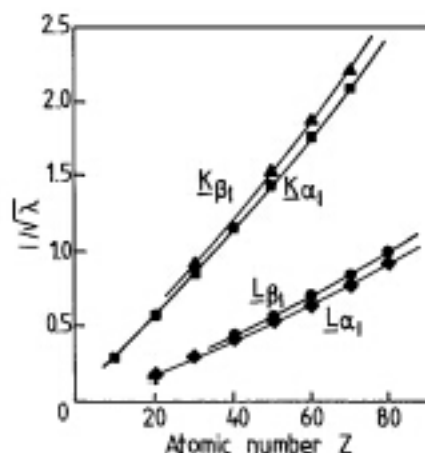


Figure 8.4 Partial Moseley's Law plots for selected K and L lines, showing the relationship between the X-ray emission wavelength and atomic number of the element. Using this relationship it was possible to predict undiscovered elements and to correctly assign atomic numbers to known elements. (From Helsen and Kuczumow, 2nd ed., used with permission.)

microprobe (Chapter 14) or a scanning electron microscope. The basic principles of each are described below.

8.1.3.1. The 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 Fig. 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 ; $I_0(\lambda)$, the incident intensity at the same wavelength; μ_m , the mass absorption coefficient (in cm^2/g); ρ , the density of the sample (in g/cm^3); and x , the sample thickness (in 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. Tables of mass absorption coefficients can be found in the text by Bertin or in handbooks listed in the bibliography.

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 and 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

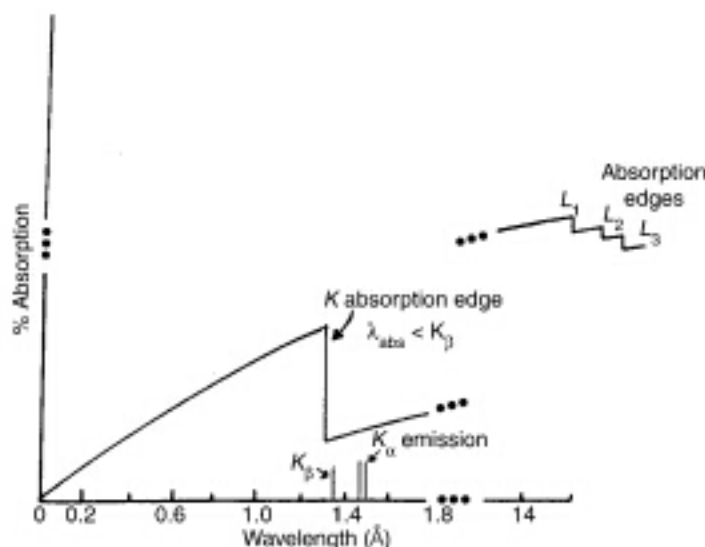


Figure 8.5 The X-ray absorption spectrum of a pure metal. Longer wavelengths are more readily absorbed than shorter wavelengths. The absorption spectrum is characterized by absorption edges, which are abrupt increases in absorption at energies sufficient to eject an electron from one of the atomic shells.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

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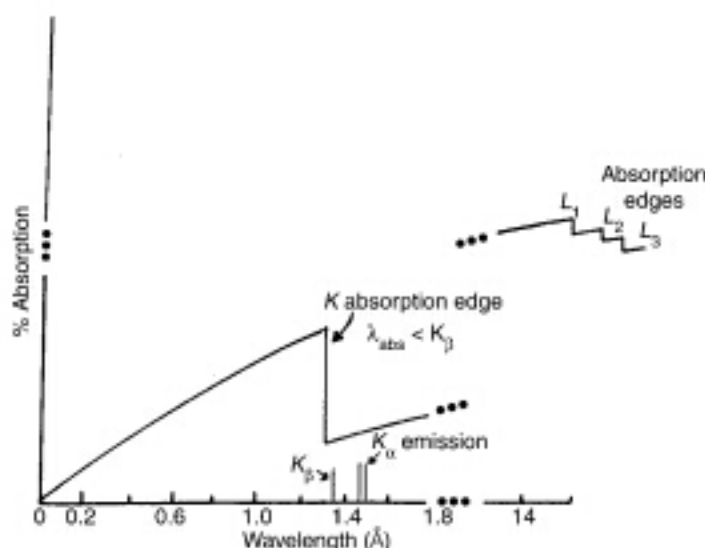


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