

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.

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 Fig. 8.5, it can be seen that radiation with a wavelength of 1.8 \AA 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 \AA . 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**. After the absorption edge, the penetrating power continues to increase as the wavelength decreases further until finally the degree of absorption is extremely small at very small wavelengths. At wavelengths less than 0.2 \AA , penetrating power is extremely great and we are approaching the properties of interstellar radiation such as cosmic rays, which have extremely high penetrating power. Wavelengths shorter than the K absorption edge have sufficient energy to eject K electrons; the bombarded sample will exhibit both continuum radiation and the characteristic K lines for the sample. This process is called XRF and will be discussed in detail. Wavelengths just slightly longer than the K absorption edge do not have enough energy to displace K electrons. The absorption spectrum is unique for each element; portions of the absorption spectrum showing the position of the K absorption edge for several pure elements are shown in Fig. 8.6.

Another way of looking at X-ray absorption is to plot the mass absorption coefficient as a function of wavelength or energy. For a thin sample of pure metal and a constant incident intensity, Eq. (8.9) indicates that if the percent absorption changes as a function of wavelength, it must be that μ_m changes. A plot of μ_m vs. X-ray energy for the element lead is shown in Fig. 8.7. The K, L, and M absorption edges are seen.

The wavelengths of the absorption edges and of the corresponding emission lines do not quite coincide. This is because the energy required to dislodge an electron from an atom (the absorption edge energy) is not quite the same as the energy released when the dislodged electron is replaced by an electron from an outer shell (emitted X-ray energy). The amount of energy required to displace the electron must dislodge it from its orbital and remove it completely from the atom. This is more than the energy released by an electron in an atom falling from one energy level to another. A few absorption edge values are given in Table 8.3. Figure 8.5 shows that the energy of the K absorption edge is greater than the energy of the K emission lines. As opposed to emission spectra, only one K absorption edge is seen per element, since there is only one energy level in the K shell. Three absorption edges of different energies are observed for the L levels, five for the M levels, and so on; these can be seen in Fig. 8.7. A comprehensive table of absorption edge wavelengths is located in Appendix 8.2.

8.1.3.2. The X-ray Fluorescence (XRF) Process

X-rays can be emitted from a sample by bombarding it with electrons or with other X-rays. When electrons are used as the excitation source, the process is called X-ray emission

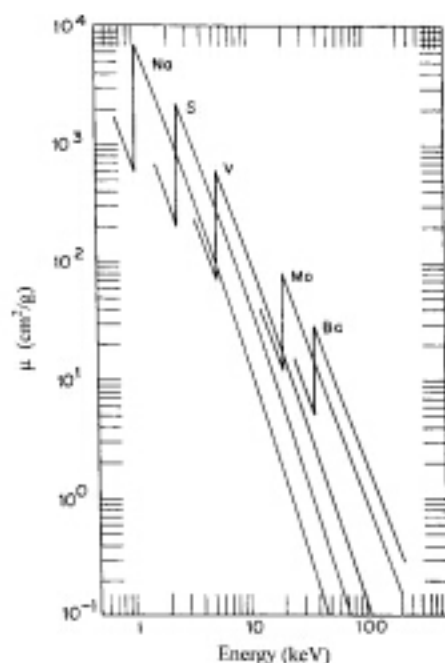


Figure 8.6 Energies of the K absorption edge for several pure elements. [Courtesy of ORTEC (Ametek) (www.ortec-online.com). From Jenkins et al., 1981, used with permission.]

This is the basis of X-ray microanalysis using an electron microprobe (Chapter 14) or a scanning electron microscope. When the excitation source is a beam of X-rays, the process of X-ray emission is called fluorescence. This is analogous to molecular fluorescence discussed in Chapter 5 and atomic fluorescence discussed in Chapter 7,

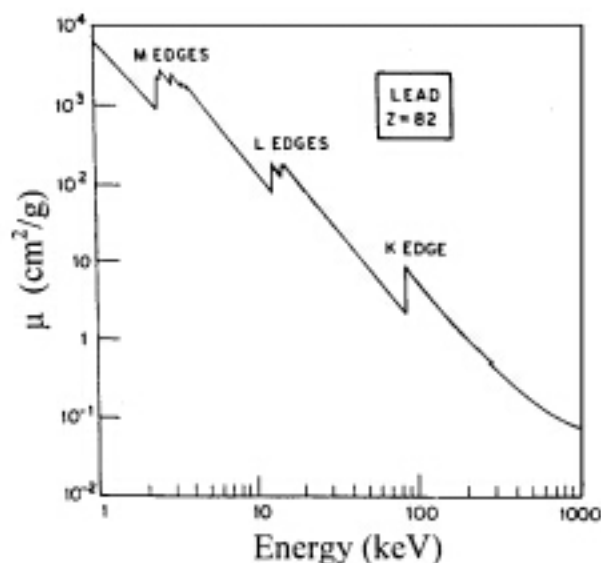


Figure 8.7 The mass absorption coefficient for Pb as a function of energy. The K, L, and M absorption edges are seen. [Courtesy of ORTEC (Ametek) (www.ortec-online.com). From Jenkins et al., 1981, used with permission.]

because the wavelength of excitation is shorter than the emitted wavelengths. The beam of exciting X-rays is called the *primary* beam; the X-rays emitted from the sample are called *secondary* X-rays. The use of an X-ray source to produce secondary X-rays from a sample is the basis of XRF spectroscopy. The primary X-ray beam must have a λ_{min} that is shorter than the absorption edge of the element to be excited.

8.1.3.3. The X-ray Diffraction (XRD) Process

Crystals consist of atoms, ions or molecules arranged in a regular, repeating 3D pattern, called a crystal lattice. This knowledge came from the pioneering work of German physicist Max von Laue and the British physicists, W.H. Bragg and W.L. Bragg. Max von Laue demonstrated in 1912 that a crystal would diffract X-rays, just as a ruled grating will diffract light of a wavelength close to the distance between the ruled lines on the grating. The fact that diffraction occurs indicates that the atoms are arranged in an ordered pattern, with the spacing between the planes of atoms on the order of short wavelength electromagnetic radiation in the X-ray region. The diffraction pattern could be used to measure the atomic spacing in crystals, allowing the determination of the exact arrangement in the crystal, the *crystal structure*. The Braggs used von Laue's discovery to determine the arrangement of atoms in several crystals and to develop a simple 2D model to explain XRD.

If the spacing between the planes of atoms is about the same as the wavelength of the radiation, an impinging beam of X-rays is reflected at each layer in the crystal, as shown in Fig. 8.8. Assume that the X-rays falling on the crystal are parallel waves that strike the crystal surface at angle θ . That is, the waves O and O' are in phase with each other and reinforce each other. In order for the waves to emerge as a reflected beam after scattering from atoms at points D and B, they must still be in phase with each other, that is, waves Y and X must still be parallel and coherent. If the waves are completely out of phase, their amplitudes cancel each other, they are said to interfere destructively, and no beam emerges. In order to get reinforcement, it is necessary that the two waves stay in phase with each other after diffraction at the crystal planes.

It can be seen in Fig. 8.8 that the lower wave travels an extra distance AB + BC compared with the upper wave. If AB + BC is a whole number of wavelengths, the emerging beams Y and X will remain in phase and reinforcement will take place. From this deduction, we can calculate the relationship between the wavelengths of X-radiation, the distance d between the lattice planes, and the angle at which a diffracted beam can emerge. We employ the following derivation.

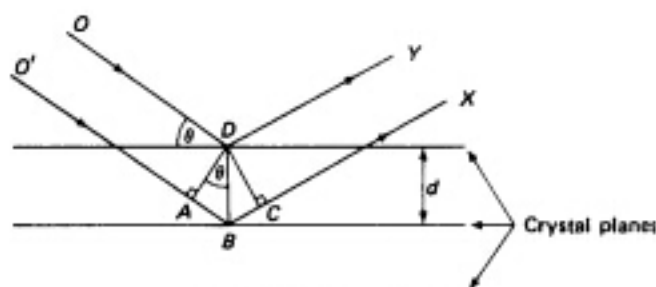


Figure 8.8 Diffraction of X-rays by crystal planes.

X-ray waves O and O' are parallel. The extra distance traveled by wave O' in traveling through the crystal is $AB + BC$. For diffraction to occur it is necessary that this distance be a whole number of wavelengths, n ; that is,

$$\text{distance } AB + BC = n\lambda \quad (8.11)$$

but

$$AB + BC = 2AB \quad (8.12)$$

and

$$AB = DB \sin \theta \quad (8.13)$$

where θ is the angle of incidence of the X-ray beam with the crystal; therefore

$$AB = d \sin \theta \quad (8.14)$$

where d is the distance between the crystal planes, called the interplanar distance. (Note from Fig. 8.8 that $d = DB$).

Therefore

$$AB + BC = n\lambda = 2AB = 2d \sin \theta$$

or

$$n\lambda = 2d \sin \theta \quad (8.15)$$

The equation $n\lambda = 2d \sin \theta$ is known as the **Bragg equation**. The important result of this equation is that at any particular angle of incidence θ , only X-rays of a particular wavelength fulfill the requirement of staying in phase and being reinforced, and are therefore diffracted by the crystal. Diffraction of X-rays by crystals forms the basis of XRD for crystal structure determination and is also the reason XRF spectrometry is possible, as will be seen.

8.2. INSTRUMENTATION

Instrumentation for X-ray spectrometry requires a source, a wavelength (or energy) selector, a detector, collimators, and filters. The component parts of the instrument are similar for XRF, XRD, and the other fields, but the optical system varies for each one. For example, in XRF spectrometry, either the energies or wavelengths of emitted X-rays are measured to characterize the elements emitting them. In the *wavelength-dispersive mode* of analysis (WDXRF), a dispersing device separates X-rays of differing wavelength by deflecting them at different angles proportional to their wavelength. In the *energy-dispersive mode* (EDXRF), there is no dispersing device, and a detector measures and records the energies of each individual detected X-ray photon.

The low energy X-rays emitted by elements with atomic numbers less than sodium ($Z < 11$) are easily absorbed by air. Therefore most X-ray systems operate either under vacuum or purged with helium. The entire spectrometer, including the source, sample, optics, and most detectors are within the vacuum/purge chamber. Liquid samples cannot be analyzed under vacuum, so most systems permit the analyst to switch from a vacuum to a helium purge as needed, usually in less than 2 min.

Commercial X-ray spectrometers may be equipped with automatic sample changers for unattended analysis of multiple samples. Computer-controlled spectrometers permit

the identification of the position of liquid samples in the sample changer, and automatically switch to a helium purge to avoid exposing the liquid samples to vacuum.

8.2.1. X-Ray Source

Three common methods of generating X-rays for analytical use in the laboratory are:

1. Use of a beam of high-energy electrons to produce a broad band *continuum* of X-radiation resulting from their deceleration upon impact with a metal target as well as element-specific X-ray *line* radiation by ejecting inner core electrons from the target metal atoms. This is the basis of the X-ray tube, the most common source used in XRD and XRF.
2. Use of an X-ray beam of sufficient energy (the primary beam) to eject inner core electrons from a sample to produce a secondary X-ray beam (XRF).
3. Use of a radioactive isotope which emits very high energy X-rays (also called gamma radiation) in its decay process.

A fourth method of producing X-rays employs a massive, high-energy particle accelerator called a synchrotron. These are available at only a few locations around the world, such as the Brookhaven National Laboratory or the Stanford Accelerator Center in the US, and are shared facilities servicing a large number of clients. X-rays may be generated when alpha particles or other heavy particles bombard a sample; this technique is called particle-induced X-ray emission (PIXE) and requires a suitable accelerator facility. The use of an electron beam to generate X-rays from a microscopic sample as well as an image of the sample surface is the basis of X-ray microanalysis using an electron microprobe or scanning electron microscopy.

These different X-ray sources may produce either broad band (continuum) emission or narrow line emission, or both simultaneously, depending on how the source is operated. Figure 8.3 displays the simultaneous generation of both a broad continuum of X-ray energies with element-specific lines superposed upon it, obtained by bombarding rhodium metal with electrons in an X-ray tube.

8.2.1.1. The X-ray Tube

A schematic X-ray tube is depicted in Fig. 8.9. The X-ray tube consists of an evacuated glass envelope containing a wire filament cathode and a pure metal anode. A thin beryllium window sealed in the glass envelope allows X-rays to exit the tube. The glass envelope is encased in lead shielding and a heavy steel jacket with an opening over the window, to protect the tube. When a cathode (a negatively charged electrode) in the form of a metal wire is electrically heated by the passage of current, it gives off electrons, a process called thermionic emission. If a positively charged metallic electrode (called an anode) is placed

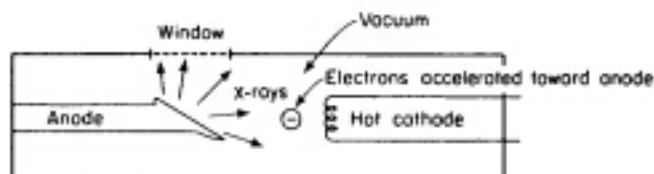


Figure 8.9 Schematic diagram of an X-ray tube.