

which is characteristic of the elements present and their concentrations in the sample. Their analytical uses are described in this section.

8.3.1. X-Ray Absorption

If the wavelength of an X-ray beam is short enough (high energy), it will excite an atom that is in its path. In other words, the atom absorbs X-rays that have enough energy to cause it to become excited. As a rule of thumb, the X-rays emitted from a particular element will be absorbed by elements with a lower atomic number. The ability of each element to absorb increases with atomic number.

Beer's Law indicates that

$$\log\left(\frac{P_0}{P_x}\right) = \mu_x \quad (8.19)$$

where μ_x is the linear absorption coefficient; x , the path length through the absorbing material; P_0 , the X-ray power before entering sample; and P_x the X-ray power leaving sample.

However,

$$\left(\frac{\mu_x}{\rho}\right) = \mu_m \quad (8.20)$$

where μ_m is the mass absorption coefficient and ρ is the density.

But

$$\mu_m = \left(\frac{CN_0Z^4\lambda^3}{A}\right) \quad (8.21)$$

where C is a constant; N_0 the Avogadro's number; Z , the atomic number; A , the atomic weight; and λ , the wavelength of the radiation.

It can be seen that at a given wavelength, μ_m is proportional to Z^4 divided by the atomic weight. This relationship is shown in Fig. 8.32. The set-up for X-ray absorption is slightly different than that for XRF, as seen in Fig. 8.33. The sample is placed directly in line with the X-ray tube, in a configuration very similar to UV/VIS absorption spectrometry. The parameter measured is the decrease in intensity of the incident

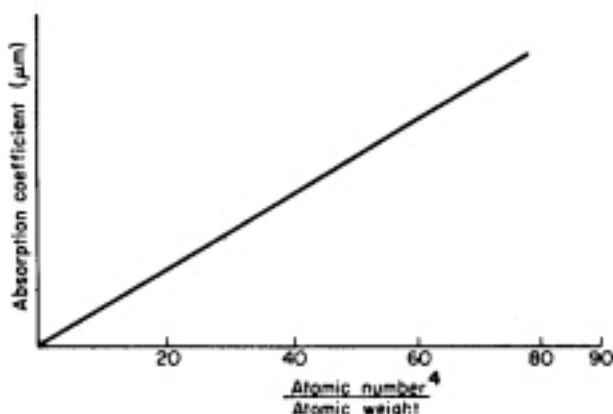


Figure 8.32 Relationship between atomic number and X-ray absorption coefficient.

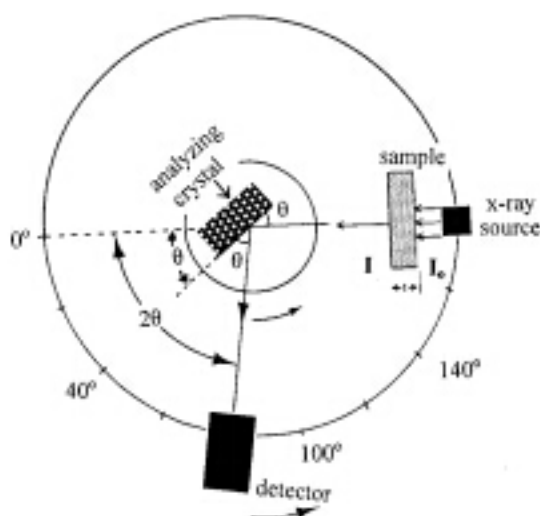


Figure 8.33 X-ray absorption. The sample is placed between the X-ray tube and the detector. The intensity of the source is I_0 . The intensity of light reaching the detector after passing through a sample of thickness t is I . I will be less than I_0 if absorption occurs.

beam after passing through the sample. The same detectors described for XRF may be used for X-ray absorption spectrometry. Older systems and current medical systems use photographic film for detection (radiography).

The most familiar example (and the oldest use) of X-ray absorption does not provide chemical information, but rather physical information. That is the use of X-ray absorption in medical radiography, but it is based on the relationship between absorption coefficient and atomic number. For example, the human arm consists of flesh, blood, and bone. The flesh or muscle is made up primarily of carbon, nitrogen, oxygen, and hydrogen. These are all low atomic number elements, and their absorptive power is very low. Similarly, blood, which is primarily water, consists of hydrogen, oxygen, plus small quantities of sodium chloride and trace materials. Again, the absorptive power of blood is quite low. In contrast, bone contains large quantities of calcium and phosphorus, primarily as calcium phosphate. The atomic numbers of these elements are considerably higher than those mentioned before, and so the absorptive power is considerably higher. When an X-ray picture is taken of an arm, the x-radiation penetrates the muscle tissue and blood quite readily, but is absorbed significantly by the bone. A photograph of this absorption indicates the location of the bone in the arm. The procedure is routinely used in medicine to detect broken bones.

Another application of X-ray absorption in medicine is to define the shapes of arteries and capillaries. Normally the blood absorbs only poorly; however, it is possible to inject a solution of strongly absorbing cesium iodide into the veins. The material is then swept along with the blood and follows the contours of the arteries. An X-ray video is recorded as the highly absorbing cesium iodide flows through the arteries, showing the contours of the arteries. This can be used to identify breaks in the veins or arteries that could cause internal bleeding. Such internal bleeding can be the cause of a stroke. The technique may also be used to indicate a buildup of coating on the inside of the veins. This is particularly dangerous in the heart, where deposits of cholesterol restrict the flow of blood through the heart. If this is left unchecked, a heart attack will result.

X-ray absorption can be used to diagnose this problem and to locate exactly the position of deposits. Surgery is made much easier by this technique.

In the field of metallurgy, applications of X-ray absorption include the detection of voids or the segregation of impurities, such as oxides, in welds and other joints. Figure 8.34 shows an idealized X-ray absorption photograph of a mechanical weld that contains voids or internal holes. Such holes indicate that the weld is mechanically weak and might break in use. If the weld is weak, it must be strengthened to form a sufficiently strong joint. This type of nondestructive testing is used to check the manufacturing quality of ships, aircraft, bridges, and buildings. It also used to check these structures during routine maintenance. X-ray absorption is routinely used for measuring the thickness of thin metal films.

The technique of X-ray absorption can also be used to determine the levels of liquids in enclosed vessels or pipes without opening or breaking them. The same process can be used to detect metal supports or metal fillings inside constructed objects as diverse as buildings and small works of art. A major advantage is that X-ray techniques are usually nondestructive. Sometimes artists paint over old paintings, using the canvas for their own work and covering unrecognized masterpieces in the process. Using X-ray absorption, it is possible to reveal the covered painting without removing the top painting. When used to examine a metal horse sold for several million dollars as an ancient Greek art piece, X-ray absorption showed that the horse contained internal metal supports and was therefore a fake. This was done without destroying the art piece, in case it had been authentic.

For elemental analysis, X-ray absorption is not particularly useful. As we saw in Eq. (8.10), the mass absorption coefficient needed for the Beer's Law calculation [Eq. (8.19)] must be calculated from the weight fractions of elements present in the sample. The weight fractions are usually unknown. Quantitative analysis by X-ray absorption is usually only used for the determination of a high atomic number element in a matrix of lower atomic number elements. Examples include the determination of lead or sulfur in hydrocarbon fuels, and the determination of Pt catalyst in polymers, where the difference in mass absorption coefficients between analyte and matrix is large. One approach to quantitative analysis using X-ray absorption is based on the measurement of the intensities of two or more monochromatic X-rays passed through the sample. This is called X-ray preferential absorption analysis or dual-energy transmission analysis. The analysis depends on the selective absorption of the transmitted X-rays by the analyte compared with absorption by the rest of the sample (the matrix). The sensitivity of the analysis also depends on the difference in mass absorption coefficients of the analyte and sample matrix for the transmitted X-rays; a big difference results in a more sensitive analysis. The analyte

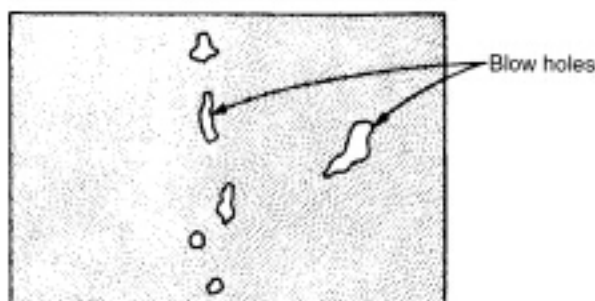


Figure 8.34 X-ray absorption photograph of a mechanical weld.

concentration calculation in any absorption method requires that the thickness and density of the sample be known and requires a homogenous matrix for accurate quantitative results.

8.3.1.1. EXAFS

A recent development in the use of X-ray absorption is a technique called EXAFS, extended X-ray absorption fine structure spectroscopy. A sample is placed in a beam of X-rays and the incident and transmitted intensities are measured as the energy of the X-ray beam is varied. A plot of the absorption vs. energy gives us the position (energy) and exact shape of the absorption edge for the element being measured. The exact energy of the absorption edge and its shape, the "fine structure", does change slightly depending on the oxidation state of the element and the number and type of nearest neighbor atoms. This change in position of the absorption edge is analogous to the chemical shift seen in NMR. EXAFS does provide oxidation state information and molecular structure information, unlike normal X-ray absorption or X-ray fluorescence, which are strictly elemental analysis techniques. Details of the spectral interpretation of EXAFS are beyond the scope of this book. The interested student can consult the text by Teo and Joy listed in the bibliography.

8.3.2. X-Ray Diffraction

X-ray diffraction or X-ray diffractometry (XRD) is a technique that is useful for the analysis of solid crystalline or semicrystalline materials. Most organic and inorganic compounds, minerals, metals, and alloys, and many types of polymers form crystals and can be analyzed by XRD. XRD can provide the exact crystal structure of a pure single crystal material. In addition, XRD can provide the qualitative and quantitative identification of the molecules present in pure crystalline powders or mixtures of crystalline powders.

The ions or molecules that make up a crystal are arranged in well-defined positions, called a crystal lattice. Figure 8.35 is an electron micrograph of the (110) plane of crystalline silicon. Three coordinates, called Miller indices, identify the plane in space; the Miller indices for this plane are 1, 1, and 0. The light spots are individual Si atoms. As can be seen, they are arranged in a very regular pattern in the 2D plane. The dark area is the empty space or interstitial space between the atoms in the lattice. A crystal is a 3D well-ordered array of atoms. An illustration of a typical crystal structure, greatly magnified, is shown in Fig. 8.36(a). As we examine the structure of the crystal, we see that the ions or atoms or molecules form planes in three dimensions. You can imagine stacking identical planes of Si atoms on top of each other to create a 3D crystal, for example.

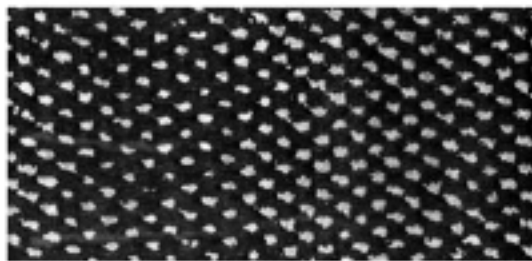


Figure 8.35 An electron micrograph of the (110) plane in crystalline silicon.

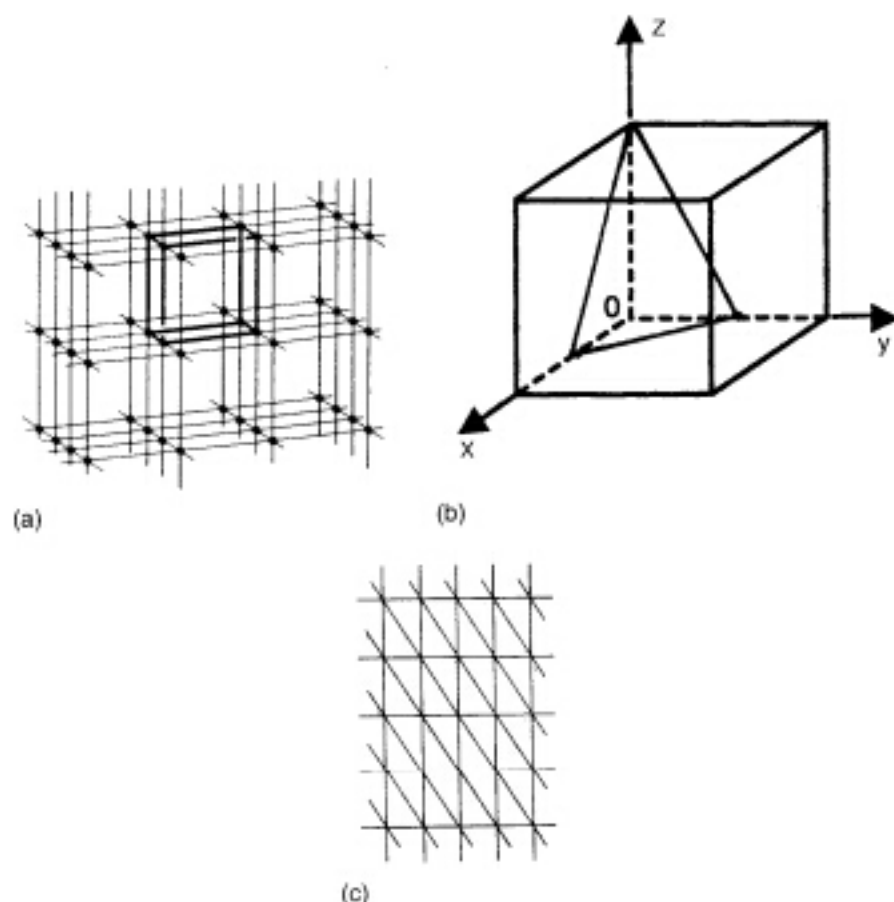


Figure 8.36 (a) A portion of a 3D crystal lattice. The unit cell, or basic repeating unit, of the lattice is shown in heavy outline. The black dots represent the atoms or ions or molecules that make up the crystal. (b) A cubic unit cell, with the corners of the cell located at 1 unit from the origin (o). The triangular plane drawn within the unit cell intersects the x -axis at $1/2$, the y -axis at $1/2$, and the z -axis at 1. This plane has Miller indices of (221). (c) A family of planes shown in a 2D lattice.

The **unit cell**, shown in heavy outline in the lattice, can be moved in three dimensions to recreate the entire crystal lattice. The unit cell is the smallest volume that can be used to describe the entire lattice. A Cartesian coordinate system is used to locate points, directions, and planes in a crystal lattice. A unit cell has its origin at the intersection of the three axes, and is designated by its edge lengths in the x , y , and z directions and by three angles. An atom (molecule or ion) in the crystal lattice is a point, identified by its x , y , and z coordinates. A plane is identified by its Miller indices, the reciprocals of the intersection points of the plane with the x -, y -, and z -axes. For example, suppose the unit cell is a cube, with edges equal to 1 unit of length on each axis as shown in Fig. 8.36(b). A triangular plane is shown within the unit cell. The plane intersects the x -axis at $1/2$, the y -axis at $1/2$, and the z -axis at 1; it has intercepts of $1/2$, $1/2$, 1. The reciprocals are 2, 2, and 1, so the Miller indices for this plane are (221). A plane that is parallel to a given axis has an intercept of infinity; the reciprocal of infinity is 0. [What axis is the (110) plane in Si parallel to? Draw the (110) plane in a cubic unit cell such as the one shown in Fig. 8.36(b)]. A crystal lattice