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 Å, penetrating power is extremely high, 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 Figure 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, Equation 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 versus X-ray energy for the element lead is shown in Figure 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, as seen in Figure 8.6b. 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 8.6b 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 Figure 8.7. A comprehensive table of absorption edge wavelengths is located in Appendix 8.B.

8.1.3.2 X-Ray Fluorescence Process

X-rays can be emitted from a sample by bombarding it with electrons, alpha particles, or with other X-rays. When electrons or alpha particles are used as the excitation source, the process is called X-ray emission or particle-induced X-ray emission (PIXE). This is the basis of X-ray microanalysis using an electron microprobe (Chapter 14) or an SEM. An alpha particle X-ray spectrometer (APXS) is currently on the Mars Curiosity rover collecting data on Martian rock composition.

When the excitation source is a beam of X-rays, that is, photons, 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, 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 X-Ray Diffraction 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
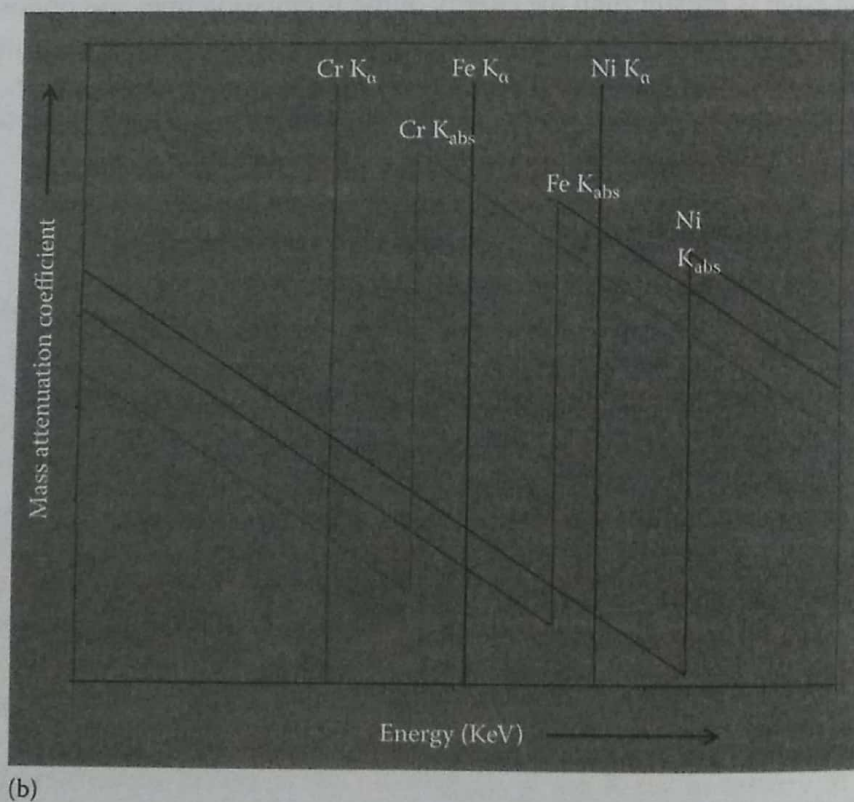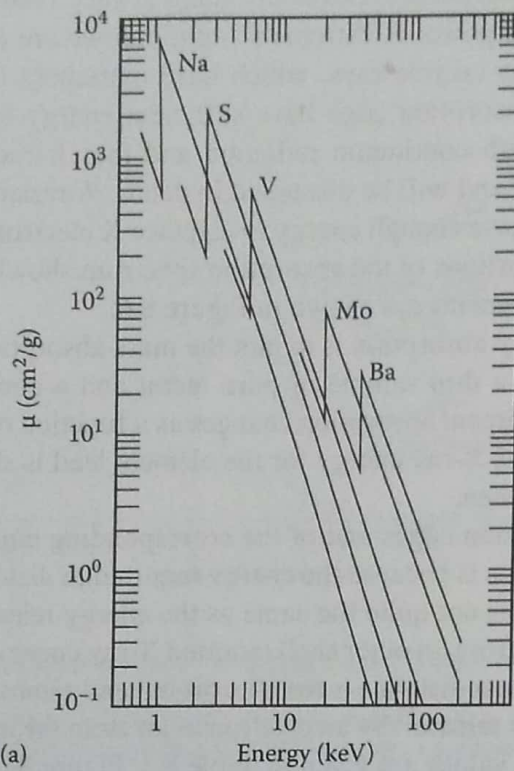
(a)

(b)

Figure 8.6 (a) Energies of the K absorption edges for several pure elements. (Courtesy of ORTEC (Ametek). www.ortec-online.com; From Jenkins, R. et al., *Quantitative X-Ray Spectrometry*, Marcel Dekker, Inc., New York, 1981. Used with permission.) (b) Energies of the K absorption edge plotted schematically for the main elements in steel. (Courtesy of the University of Western Ontario XRF Short Course, London, Ontario, Canada.)
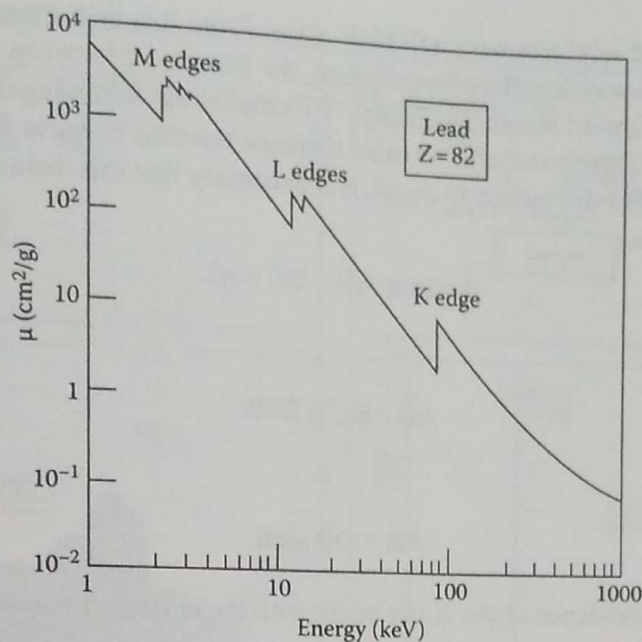
Figure 8.7 The mass absorption coefficient for Pb as a function of energy. The K, L, and M absorption edges are seen. (Courtesy of ORTEC (Ametek). www.ortec-online.com; From Jenkins, R. et al., *Quantitative X-Ray Spectrometry*, Marcel Dekker, Inc., New York, 1981. Used with permission.)

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 Figure 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 B and D, 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 Figure 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
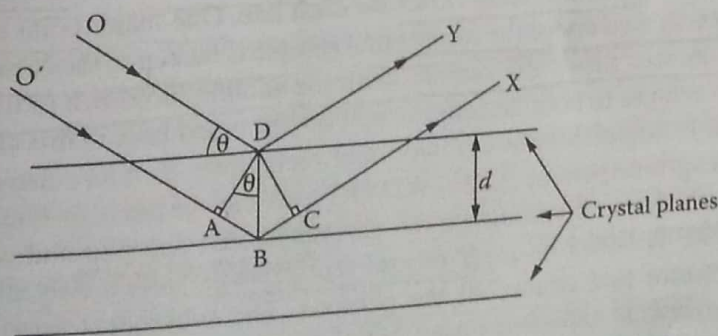

Figure 8.8 Diffraction of X-rays by crystal planes.

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.

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,

$$\text{distance } AB + BC = n\lambda \tag{8.11}$$

but

$$AB + BC = 2AB \tag{8.12}$$

and

$$AB = DB \sin\theta \tag{8.13}$$

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

$$AB = d \sin\theta \tag{8.14}$$

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

Therefore

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

or

$$n\lambda = 2d \sin\theta \tag{8.15}$$

Conclusion:
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 X-RAY FLUORESCENCE

Instrumentation for X-ray spectrometry requires a source, a wavelength (or energy) selector, a detector, and beam conditioners. Component parts of the instrument are similar for XRF, XRD, and the other fields, but the optical system varies for each one. One major point to note is that some systems have the source located above the sample (the sample is faceup to the X-ray beam); other systems have the source located below the sample, with the sample facedown to the beam. There are advantages and disadvantages to both designs, as will be discussed later in this chapter.

Generally, we can distinguish between two main techniques in XRF, energy-dispersive XRF (EDXRF) and wavelength-dispersive XRF (WDXRF), as can be seen in Figure 8.9. EDXRF is based on a detector, which can discriminate the various photon energies and count them individually, whereas WDXRF is based on a set of analyzer crystals, which only diffract one energy/wavelength into a detector that counts all the photons. The subsequent instrumentation section will illustrate the components and setups used in today's commercially available instrumentation. EDXRF is sometimes called EDX or energy-dispersive spectroscopy (EDS). It must be stressed that
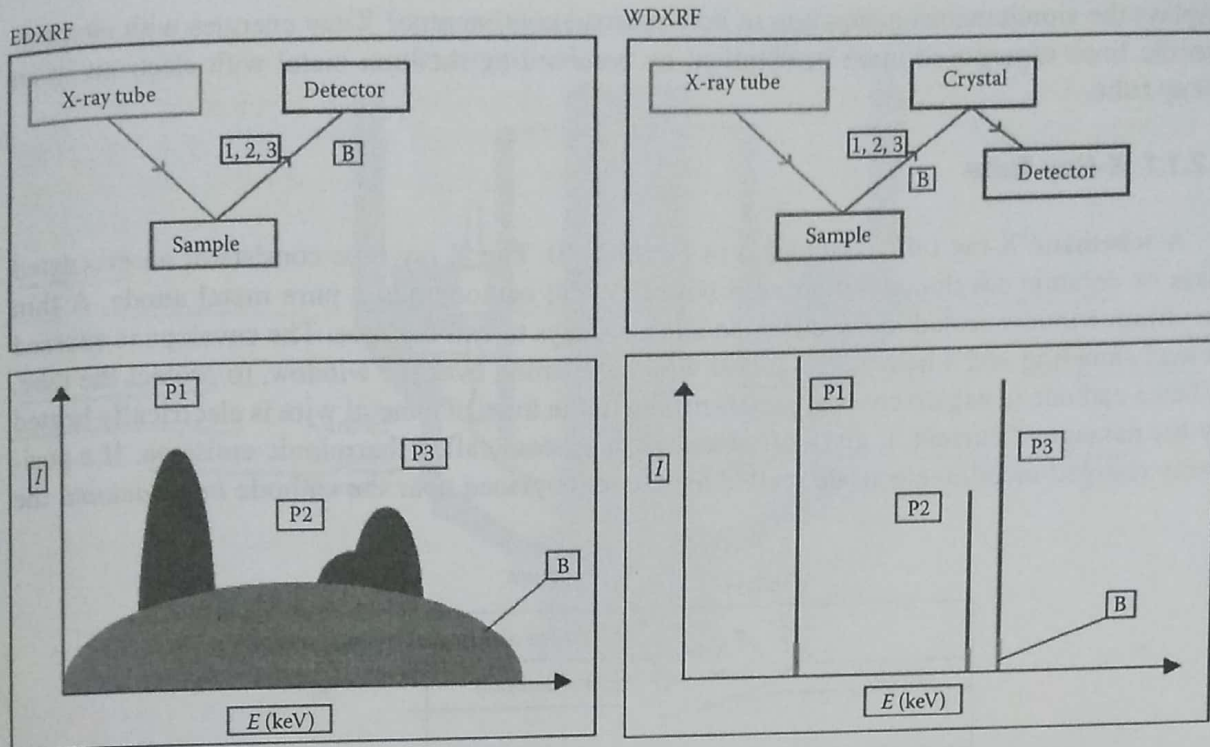
EDXRF WDXRF

Figure 8.9 Schematic comparison of EDXRF and WDXRF. The upper squares show the differences in instrument configuration, while the lower squares show the resulting spectra. B indicates the background radiation, while 1, 2, and 3 (P1, P2, P3) are photons of different energies.

Safety precautions:

all X-ray systems use ionizing radiation, which poses significant health hazards. X-ray systems of all types are regulated, and commercial systems have the proper shielding and safety interlocks to comply with regulatory requirements and prevent accidental exposure to radiation.

8.2.1 X-Ray Source

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

1. Use of a beam of high-energy electrons to produce a broadband *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

4- Method:

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 United States, 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 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 broadband (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 X-Ray Tube

A schematic X-ray tube is depicted in Figure 8.10. The X-ray tube consists of an evacuated glass or ceramic envelope containing a wire filament cathode and a pure metal anode. A thin beryllium window sealed in the envelope allows X-rays to exit the tube. The 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 near the cathode *in a vacuum*, the
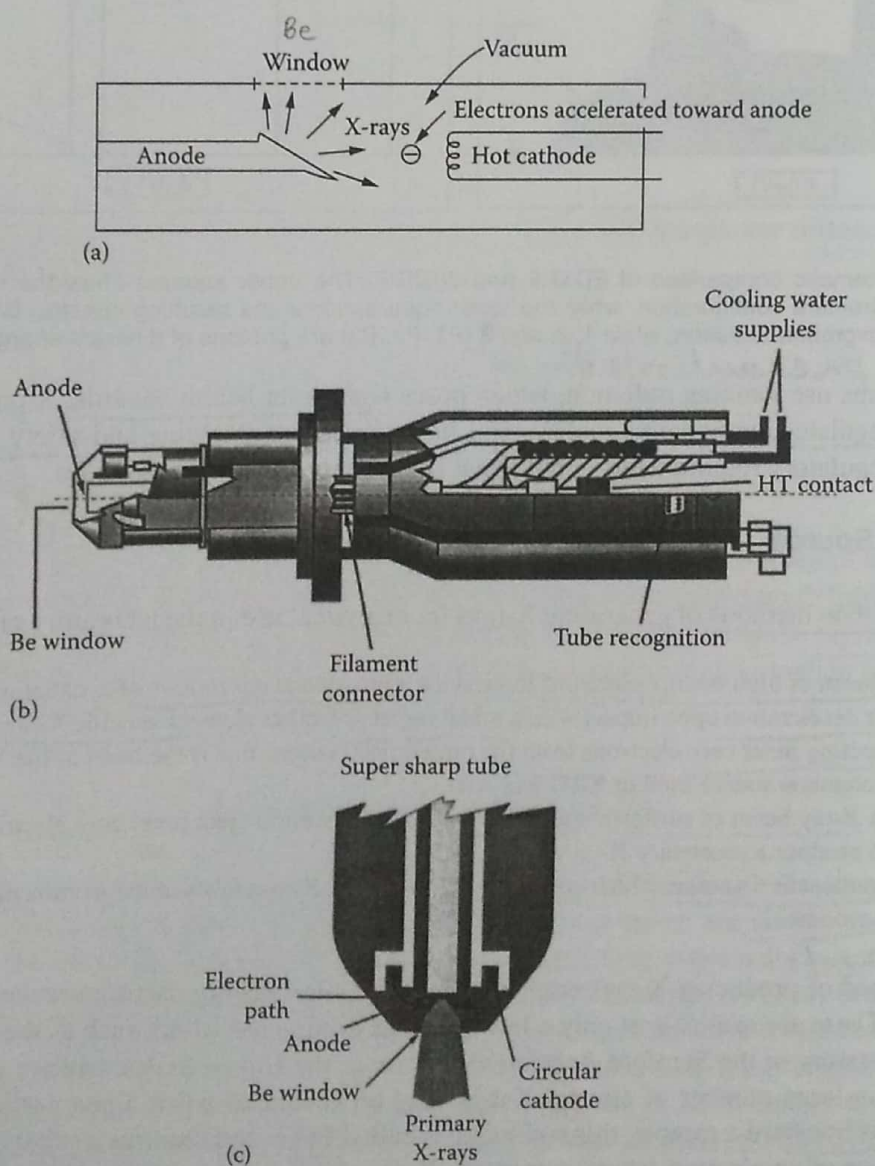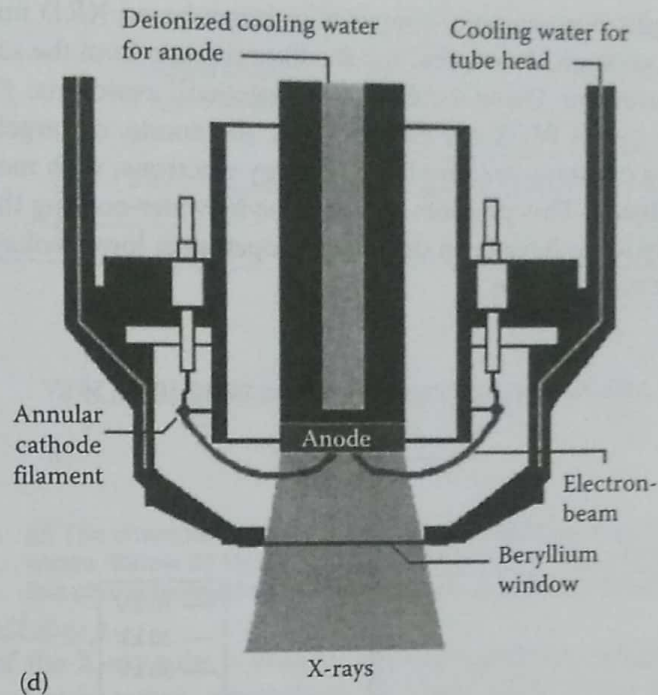

Figure 8.10   (a) Schematic diagram of a side-window X-ray tube used for XRD. (b) Schematic of the 4.0 kW ceramic end-window X-ray tube, called the Super Sharp Tube™. (c) Close-up of the window end of the Super Sharp Tube, showing the circular cathode design of this tube. (b and c: Courtesy of PANalytical, Inc., The Netherlands, www.panalytical.com.).

Figure 8.10 (continued)   (d) Schematic side view of an end-window X-ray tube showing the Be window and cooling water. (© 2013 Bruker, Inc., www.bruker.com. Used with permission.)

negatively charged electrons will be accelerated toward the anode. Upon striking it, the electrons give up their energy at the metallic surface of the anode. If the electrons have been accelerated to a high enough velocity by a sufficiently high voltage between the cathode and anode, energy is released as radiation of short wavelength (0.1–100 Å), called x-radiation or X-rays. X-ray tubes are generally operated at voltage differentials of 2–100 kV between the wire filament cathode and the anode. ε lectrodes: voltage:

   The cathode is normally a tungsten-based wire filament. The anode is called the target. The X-ray tube is named for the anode; a copper X-ray tube has a copper anode, a rhodium tube has a rhodium anode, a tungsten tube has a tungsten anode; all have tungsten-based wire cathodes. The target is usually not a solid metal but a copper slug coated with a layer of the desired target material. Numerous metals have been used as target materials, but common target elements are titanium, copper, chromium, molybdenum, rhodium, gold, silver, palladium, and tungsten. The target material determines the characteristic emission lines and affects the intensity of the continuum. The voltage between the anode and cathode determines how much energy the electrons in the beam acquire, and this in turn determines the overall intensity of the wide range of X-ray intensities in the continuum distribution and the maximum X-ray energy (shortest wavelength or λ_{min}, as shown by the Duane–Hunt law, Equation 8.7). Figure 8.11 shows how both the intensity of the continuum radiation and the short-wavelength/high-energy cutoff vary as the applied voltage to this silver (Ag) X-ray tube varies. This illustration also shows that the Ag L line emission varies as a function of the excitation. Requirement: $V \propto Ee^- \propto I$ of x.ray

   In choosing the element to be used for the target, it should be remembered that it is necessary for the energy of the X-rays emitted by the source to be greater than that required to excite the element being irradiated in an XRF analysis. As a simple rule of thumb, the target element of the source should have a greater atomic number than the elements being examined in the sample. This ensures that the energy of radiation is more than sufficient to cause the sample element to fluoresce. This is not a requirement in X-ray absorption or XRD, where excitation of the analyte atoms is not necessary. In XRD, the target is chosen to avoid the excitation of characteristic X-ray (XRF)

emissions from the sample. For example, copper (Cu) target-based XRD units can excite the iron (Fe) commonly found in geological samples, and the fluorescence from the sample will increase the background of the measurement. Using a cobalt (Co) target will avoid this. *problem:*

In many high-power (>200 W) X-ray tube designs, the anode, or target, gets very hot in use because it is exposed to a constant stream of high-energy electrons, with most of the energy being dissipated as heat on collision. This problem is overcome by water-cooling the anode. Modern low-power and compact X-ray tubes have been designed to operate at lower voltages and do not require any liquid-based cooling of the anode.
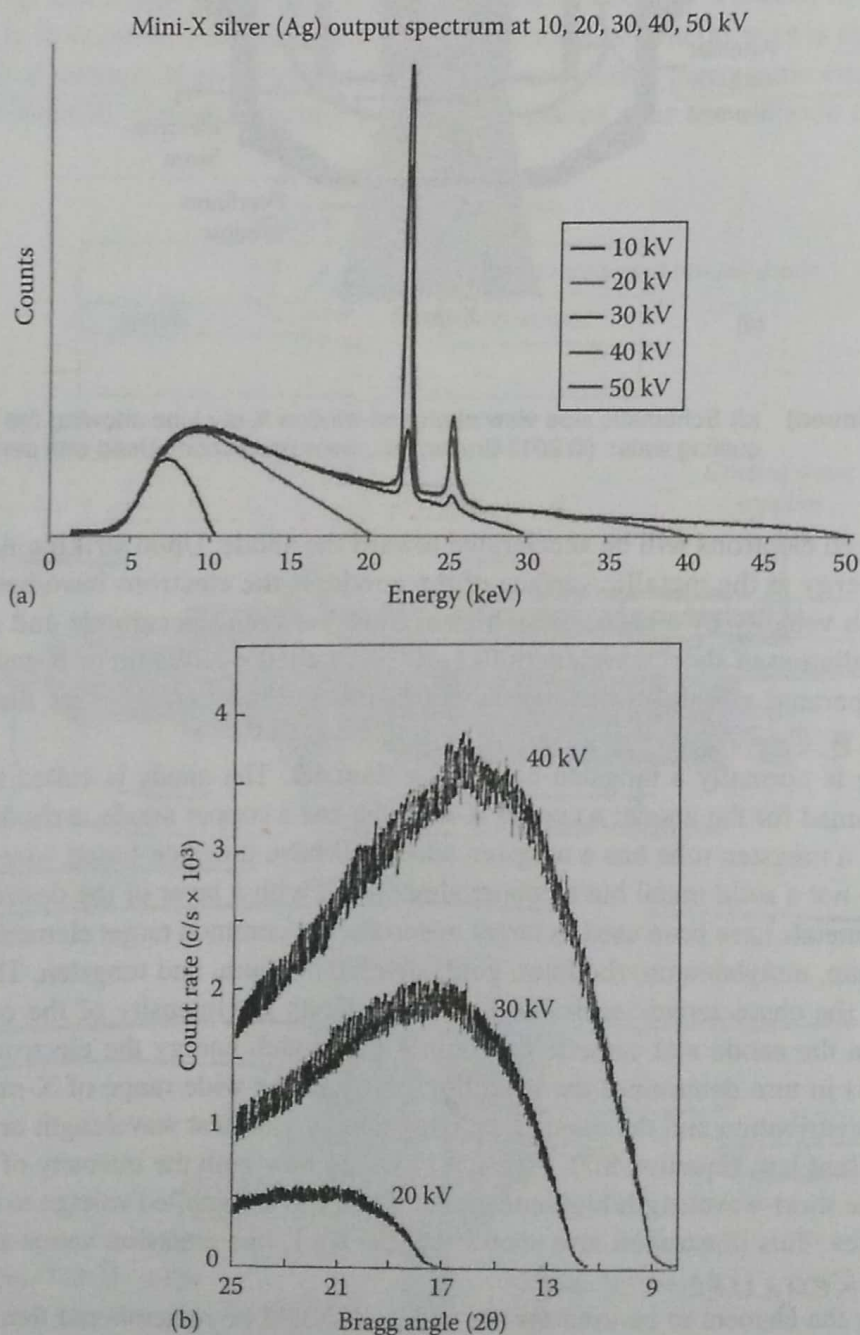

Figure 8.11 (a) Amptek Mini-X silver output spectrum at various voltages. Ten kV starts on the left side of the diagram; the curves increase in voltage moving from left to right. Below 30 kV, only continuum radiation is seen. The high-energy cutoff increases as the voltage increases, and the Ag L line emission intensity increases with voltage. (Courtesy of Amptek, Inc., Bedford, MA, www.amptek.com.) (b) The intensity of the continuum radiation from an X-ray tube and the short-wavelength cutoff vary as the applied voltage varies. This plot is of a tungsten X-ray tube.
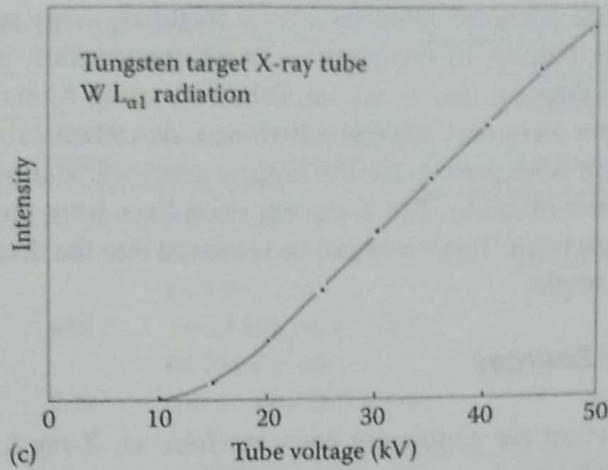
Figure 8.11 (continued)   (c) The characteristic radiation from an X-ray tube also varies as the applied voltage varies. Below 20 kV, the intensity of the tungsten L_{α_1} line is very low. The intensity of this characteristic line increases as the applied voltage increases.

Be - window:

The exit window of the X-ray tube is usually made of beryllium, which is essentially transparent to X-rays. The Be window is thin, generally 0.3–0.5 mm thick, and is very fragile. The window may be on the side of the tube, as shown in Figure 8.10a, or in the end of the tube (Figure 8.10b through d). Side-window tubes are common, but end-window tubes permit the use of a thinner beryllium window. This makes end-window tubes good for low-energy X-ray excitation by improving the low-energy output of the tube. To minimize the tube size, a transmission target can be used. The target is a layer of the target element on the beryllium window. For example, a silver transmission target can be constructed from a 0.75 μm thick layer of Ag on a 127 μm thick Be window. Figure 8.12 shows both the schematic of a side and transmission target rhodium X-ray tube.
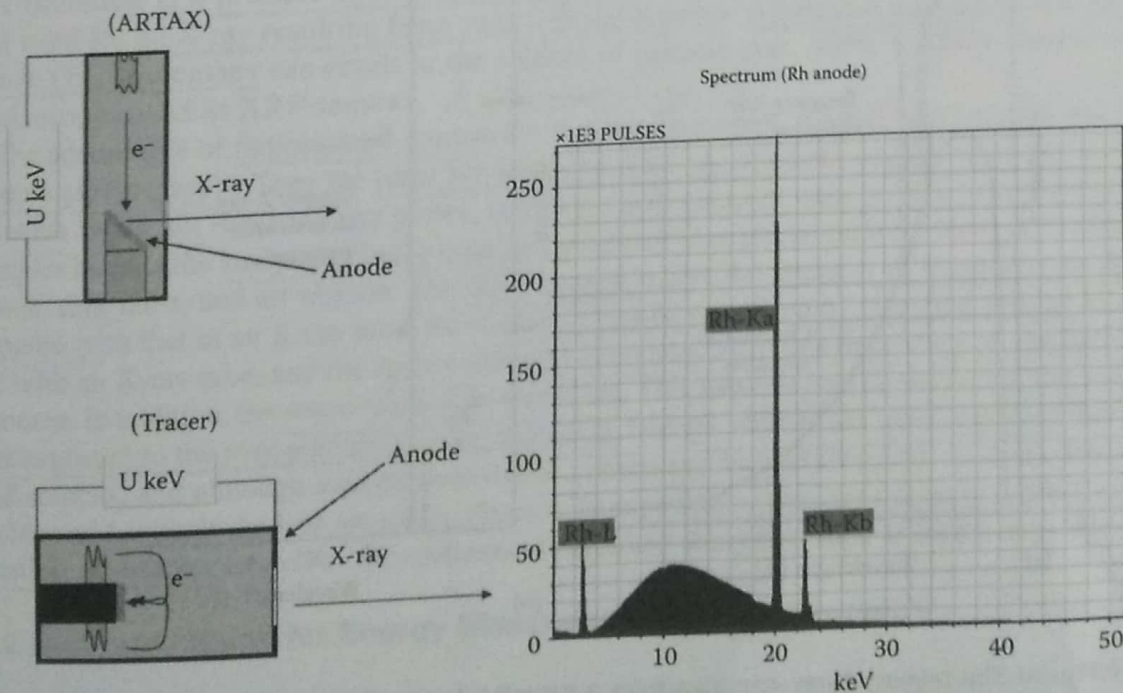

Figure 8.12   Schematic diagrams of a Rh target side-window tube (ARTAX system) and a modern hand-held transmission target design (TRACER system). (Courtesy of Roald Tagle, BRUKER NANO GmbH, Berlin, Germany. © 2013 Bruker, Inc. Used with permission.)

Precautions :

X-ray tubes must provide adequate intensity over a relatively wide spectral range for XRF in order to excite a reasonable number of elements. In some applications, monochromatic or nearly monochromatic X-rays are desired; that is accomplished by using filters or a monochromator as described later or by using a secondary fluorescent source, described subsequently. The tube output must be stable over short time periods for the highest precision and over long time periods for accuracy without frequent recalibration. The X-ray emission lines from the anode element must not interfere with the sample spectrum. Tube lines can be scattered into the detector and be mistaken for an element present in the sample.

8.2.1.2 Secondary XRF Sources

If it is necessary to prevent the continuum emission from an X-ray tube from scattering on a sample, a standard tube can be used to excite another pure metal target. The resulting XRF from the secondary target is used as the source of X-ray excitation for the sample. Such an example is shown in Figure 8.13. A standard tungsten X-ray tube is used to produce the emission spectrum on the left, with the tungsten characteristic lines superimposed on the continuum radiation. The radiation from this tube is used to strike a secondary pure copper target. The resulting emission from the copper is the copper XRF spectrum on the right.

This source emits very little or no continuum radiation but does emit quite strongly at the copper K and L lines. Of course, the metal used in the target of the first source must have a higher atomic number than copper to generate fluorescence. The Cu lines then can be used as an excitation source, although the intensity of the secondary source is much less than that of a Cu X-ray tube. However,
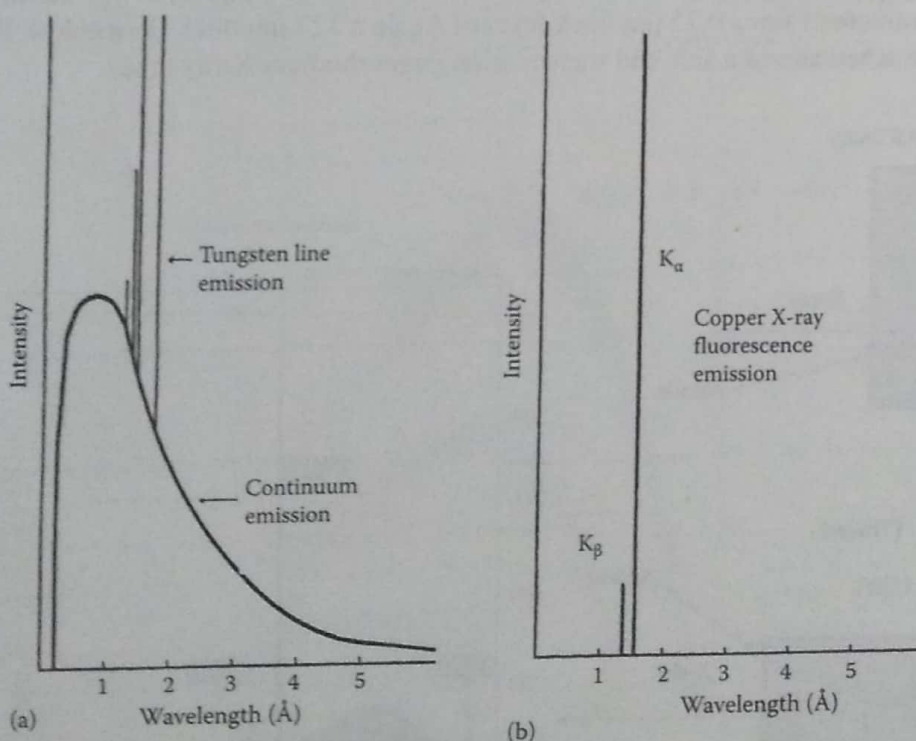
1° target z > 2° target z

Figure 8.13 (a) The primary X-ray emission from a tungsten target. (b) The secondary emission from a copper target. Note the removal of the continuum radiation and the nearly monochromatic output from the secondary target. (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.)

Table 8.4 Characteristics of Radioisotope Sources for XRF Spectrometry

Isotope	Primary Decay Mode	Half-Life (Years)	Useful Photon Energies Emitted	% Theoretical Yield (Photons per 100 Decay Transformations)	Typical Activity (mCi)
^{55}Fe	EC	2.7	5.9, 6.4 keV Mn K X-rays	28.5	5–100
^{109}Cd	EC	1.3	22.2–25.5 keV Ag K X-rays	102	0.5–100
			88.2 keV γ-ray	4	
^{241}Am	Alpha	458	14–21 keV Np L X-rays	37	1–50
			59.6 keV γ-ray	36	
^{57}Co	EC	0.74	6.4, 7.1 keV Fe K X-rays	51	1
			14.4 keV γ-ray	8.2	
			122 keV γ-ray	88.9	
			136 keV γ-ray	8.8	
^{3}H[a]	Beta	12.3	Bremsstrahlung source, endpoint at 18.6 keV		3000–5000
^{147}Pm	Beta	2.6	Bremsstrahlung source, endpoint at 225 keV		500

Source: Table from Jenkins, R. et al., *Quantitative X-Ray Spectrometry*, Marcel Dekker, Inc., New York, 1981. Used with permission.

[a] Radioactive tritium gas is adsorbed on nonradioactive metal foil, such as titanium foil.

when monochromatic or nearly monochromatic radiation is required, the loss of intensity is more than offset by the low background from the secondary source.

8.2.1.3 Radioisotope Sources

X-radiation is a product of radioactive decay of certain isotopes. The term gamma ray is often used for an X-ray resulting from such a decay process. Alpha and beta decay and electron capture (EC) processes can result in the release of gamma rays. Table 8.4 lists some common radioisotopes used as XRF sources. *Advantages:*

The advantages of radioisotope sources are that they are small, rugged, and portable and do not require a power supply. They are ideal for obtaining XRF spectra from large samples or field measurements while not requiring any power, enabling small compact units with long operation times. Examples include the analysis of bulky objects that cannot have pieces cut from them, such as aircraft engines, ship hulls, and art objects. The disadvantage is that the intensity of these sources is weak compared with that of an X-ray tube, the source cannot be optimized by changing voltage as can be done with an X-ray tube, and the source intensity decreases with time depending on the half-life of the source. In addition, the source cannot be turned off. This requires care on the part of the analyst to avoid exposure to the ever-present ionizing radiation. Isotope sources are more regulated than tube-based sources, and although isotope sources are convenient for portable XRF systems, tube-based portable and handheld devices are more common. Isotope source uses are currently limited to K line excitation approaches as well as for economical dedicated analyzers, such as for Pb in paint.

8.2.2 Instrumentation for Energy Dispersive X-Ray Spectrometry

In EDXRF spectrometry, there is no physical separation of the fluorescence radiation from the sample. There is no dispersing device prior to the detector. All the photons of all energies arrive at the detector simultaneously. Any EDXRF is designed around the following components—a source of primary excitation, a sample holder, and a detector, seen in Figure 8.14.
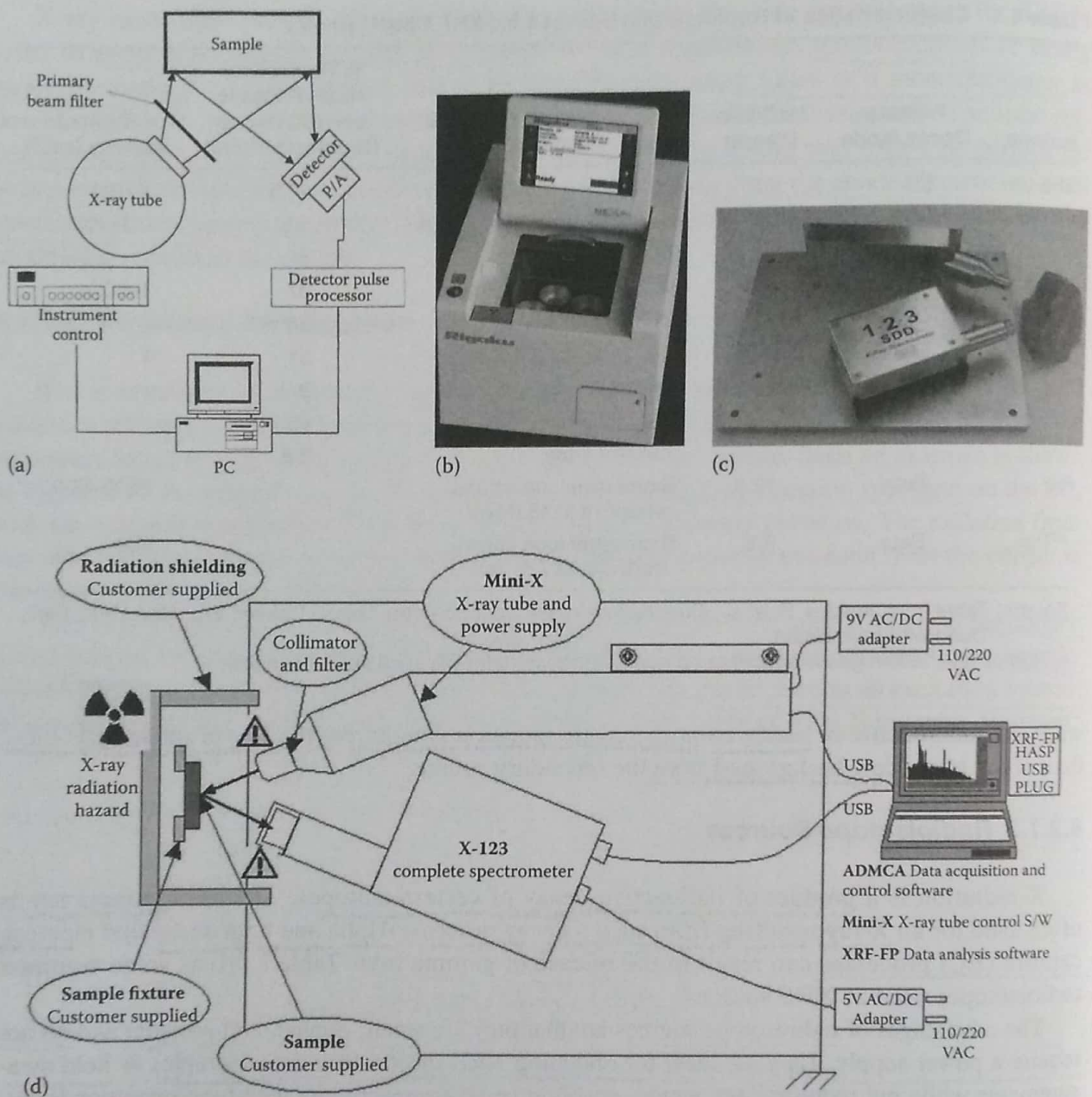
(a)   PC   (b)   (c)

(d)

Figure 8.14   (a) A schematic EDXRF system with an X-ray tube source. There is no dispersion device between the sample and the detector. Photons of all energies are collected simultaneously. (From Ellis, A.T., 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.) (b) A commercial benchtop EDXRF spectrometer, the Rigaku NEX QC, setup to measure sulfur in crude oil. (Courtesy of Applied Rigaku Technologies, Inc., Austin, TX, www.rigakuedxrf.com.) (c) Component-based compact XRF kit, showing relative positions of the X-ray tube (top), the sample (right), and the X-ray spectrometer (bottom). (d) The compact component kit as part of a complete XRF system. (c and d: Courtesy of AMPTEK, Inc. www.amptek.com.)

Controlling excitation:

All EDXRF systems are able to modify the primary signal to control the excitation of the sample. This is achieved by different means, which result in three groups of systems: direct excitation, secondary or 3D excitation, and total reflectance XRF (TXRF). *Direct excitation:*

In direct excitation systems, the source is directed toward the sample thus exciting the sample directly with the radiation from the target or isotope source (Figure 8.15). To modify the excitation or attenuate undesired parts of the excitation spectra, primary beam filters are used. To reduce the spot size and enable "micro" spot analysis, pinhole masks are in use as well. For micro spots below
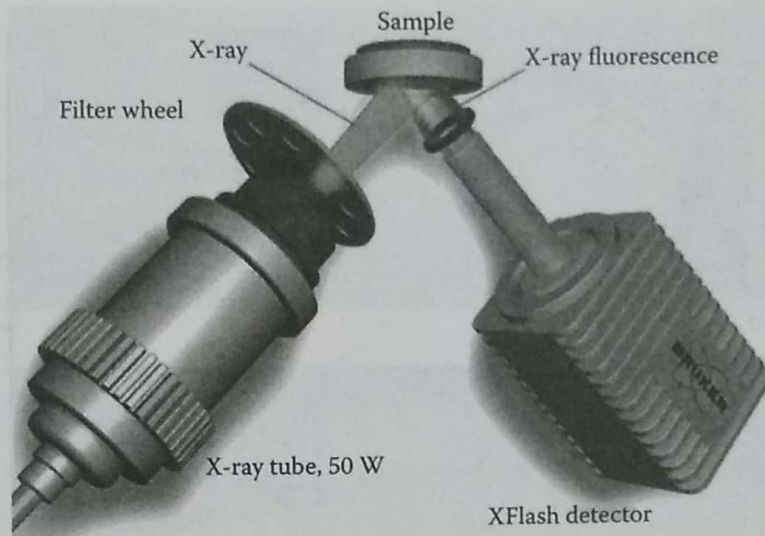
Figure 8.15   Schematic 3D view of a direct excitation EDXRF system. (© 2013 Bruker, Inc. www.bruker.com. Used with permission.)

100 µm in certain units, capillary optics are used. Typical direct excitation units are all handheld units, isotope-based units, the majority of low-power and medium-power benchtop EDXRF systems, as well as the micro-XRF and dedicated plating thickness XRF units. *Secondary excitation*

In secondary excitation units, the source is used to illuminate a selectable secondary target, which is made of specific material to either scatter the beam or to act as a new "source." The geometric arrangement is such that the signal from the secondary target illuminates the sample and also ensures that the X-ray beam is polarized (Figure 8.16). *Total Reflectance excitation*

TXRF systems use a secondary target and the principle of Bragg diffraction to create a more monochromatic beam. This beam is directed at very low incident angle to the sample to achieve "total reflectance." The signal from the sample, which has to be prepared as very thin film or
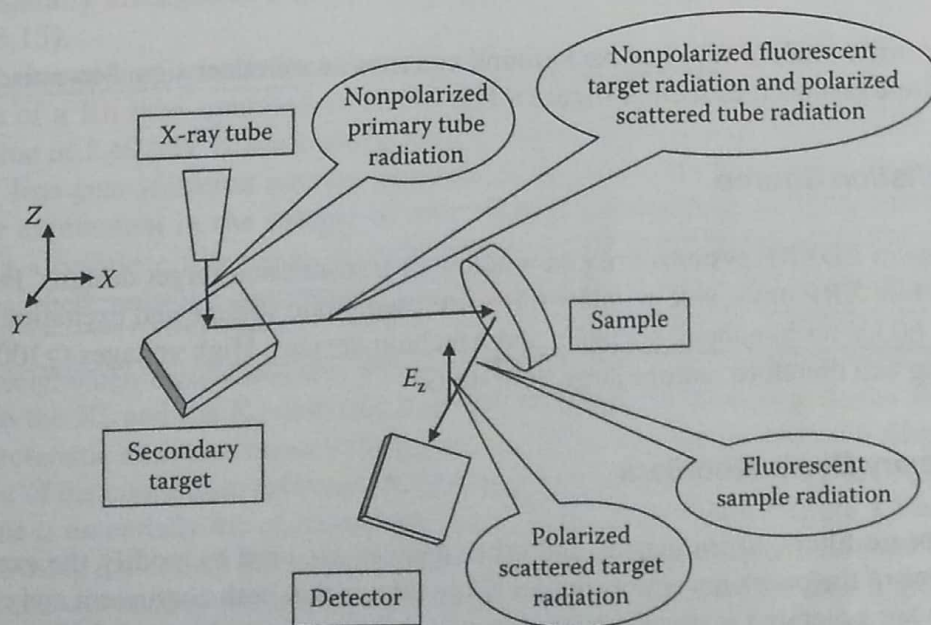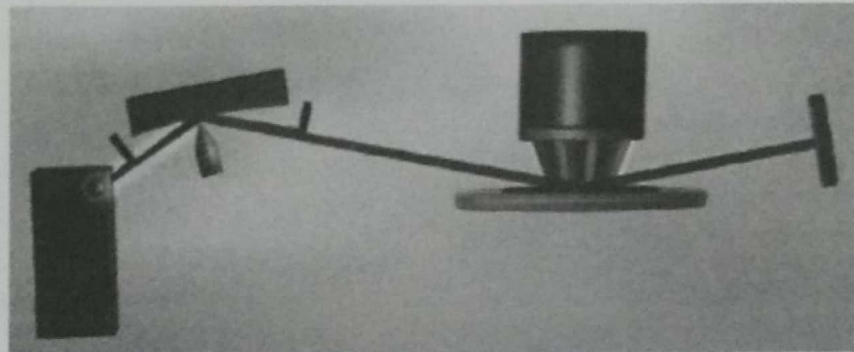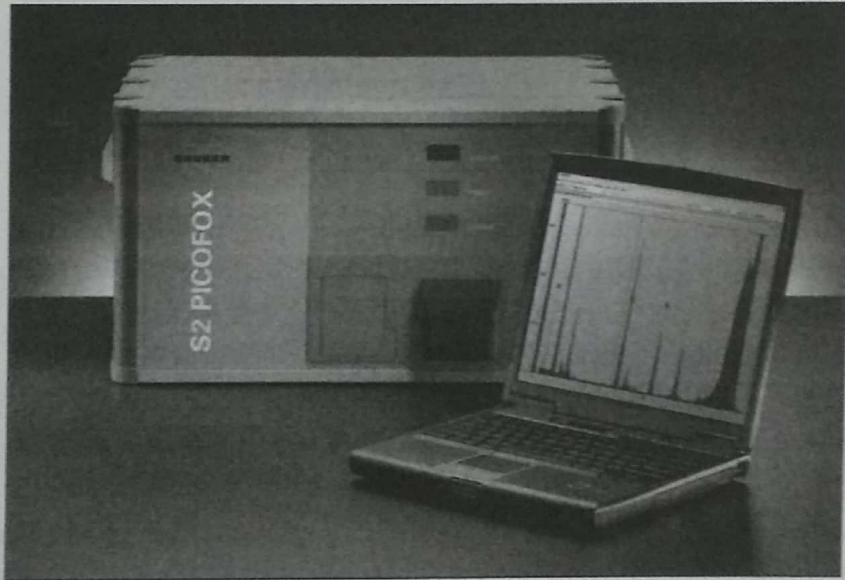

Figure 8.16   Schematic drawing of a 3D beam of a secondary target EDXRF system. (Modified from a diagram provided by Bruno Vrebos, 2009, PANaltyical Inc., The Netherlands. www.panalytical.com.)

(a)

(b)

Figure 8.17 (a) Schematic drawing of a TXRF system. From left to right is the X-ray source, the synthetic multilayer monochromator (Section 8.2.3.2), the thin sample on a support, the silicon drift detector (SDD) above the sample, and finally a beam stop. (b) A commercial TXRF spectrometer, the Bruker S2 PICOFOX with its laptop computer. The displayed spectrum shows the high S/N ratio. (© 2013 Bruker, Inc. www.bruker.com. Used with permission.)

micropowder, will exhibit a very low background and thus an excellent signal-to-noise ratio. These systems are quite compact, as seen in Figure 8.17b.

8.2.2.1 Excitation Source

Most tubes in EDXRF systems are end-window or transmission target designs. For secondary target and mobile XRF units, side-window tubes are used. Tube voltage and excitation is limited to usually 50 or 60 kV for handheld, portable, and benchtop devices. High voltages ($\geq$100 kV) require more shielding and therefore require large floor units.