near the cathode *in a vacuum*, the 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 very short wavelength (0.1–100 Å), called X-radiation or X-rays. X-ray tubes are generally operated at voltage differentials of 4–50 kV between the wire filament cathode and the anode.

The cathode is normally a tungsten 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 and a tungsten wire cathode, a rhodium tube has a rhodium anode and a tungsten wire cathode, a tungsten tube has a tungsten anode and a tungsten wire cathode. Numerous metals have been used as target materials, but common target elements are copper, chromium, molybdenum, rhodium, gold, silver, palladium, and tungsten. The wavelengths of the X-ray line radiation emitted by the target depend on the metal used. 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). Figure 8.10 shows how the intensity of the continuum radiation from a tungsten tube and the short wavelength cutoff vary as the applied voltage to the tube varies. Figure 8.11 displays the variation in intensity of one of the characteristic tungsten lines from a tungsten X-ray tube as the applied voltage is changed.

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

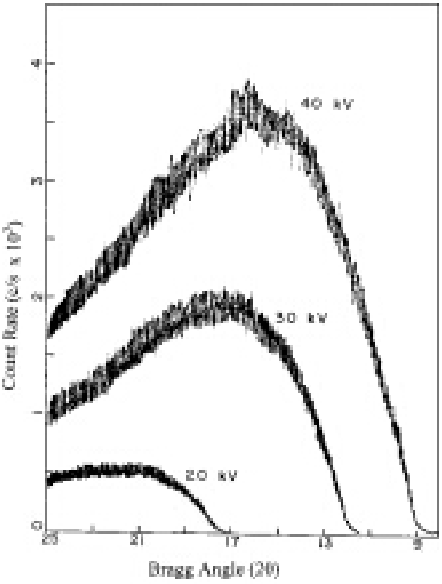

Figure 8.10 The intensity of the continuum radiation from an X-ray tube and the short wavelength cut-off vary as the applied voltage varies. This plot is of a tungsten X-ray tube.

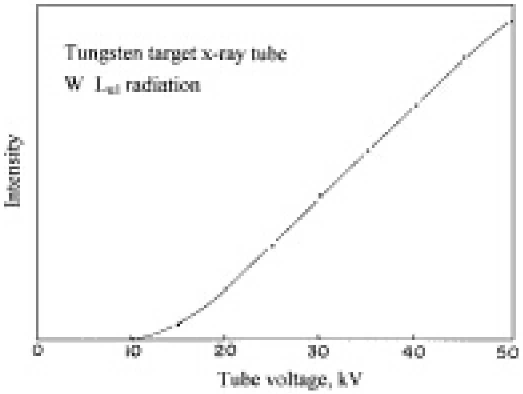

Figure 8.11 The characteristic radiation from an X-ray tube also varies as the applied voltage varies. Below 20 kV, the intensity of the tungsten L_{α_1} line is very low. The intensity of this characteristic line increases as the applied voltage increases.

absorption or XRD, where excitation of the analyte atoms is not necessary. In many 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 X-ray tubes have been designed to operate at lower voltages and do not require water-cooling of the anode.

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 Fig. 8.9, or in the end of the tube. 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. A commercial end-window tube is depicted in Fig. 8.12(a). Figure 8.12(b) shows a close up of the anode and cathode designs in this tube.

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 below 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 falling 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 Fig. 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.

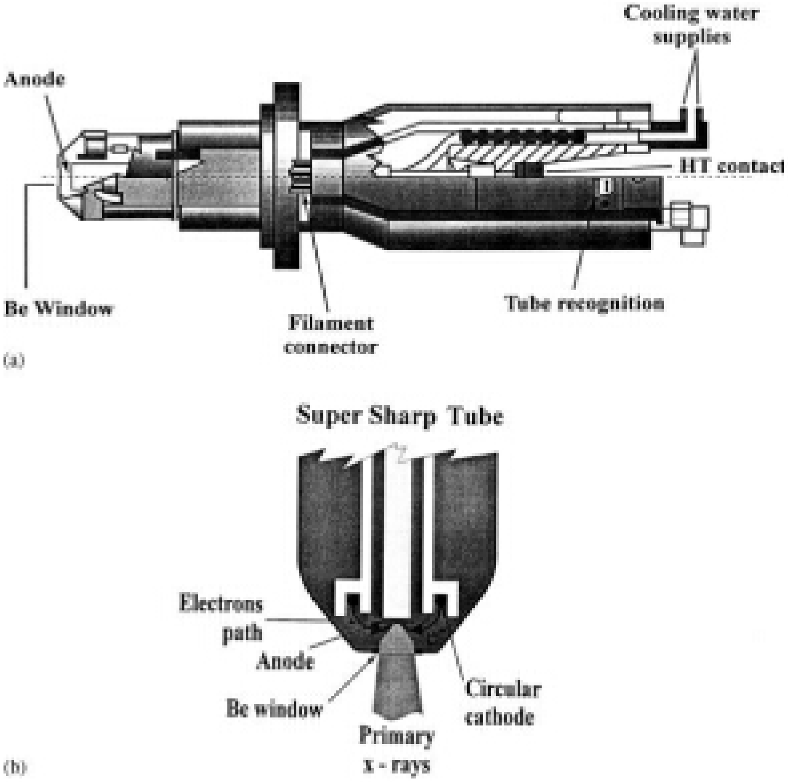

Figure 8.12 (a) Schematic of the 4.0 kW ceramic end window X-ray tube, called the Super Sharp Tube™. (b) Close up of the window end of the Super Sharp Tube™, showing the circular cathode design of this tube. [Courtesy of PANalytical, Inc., The Netherlands (www.panalytical.com).]

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, 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 processes can result in the release of gamma rays. Table 8.4 lists some common radioisotopes used as XRF sources.

The advantages of radioisotope sources are that they are small, rugged, portable, and do not require a power supply. They are ideal for obtaining XRF spectra from bulky samples that do not fit into conventional spectrometers (and cannot have pieces cut from them), such as aircraft engines, ship hulls, art objects, and the like. 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,

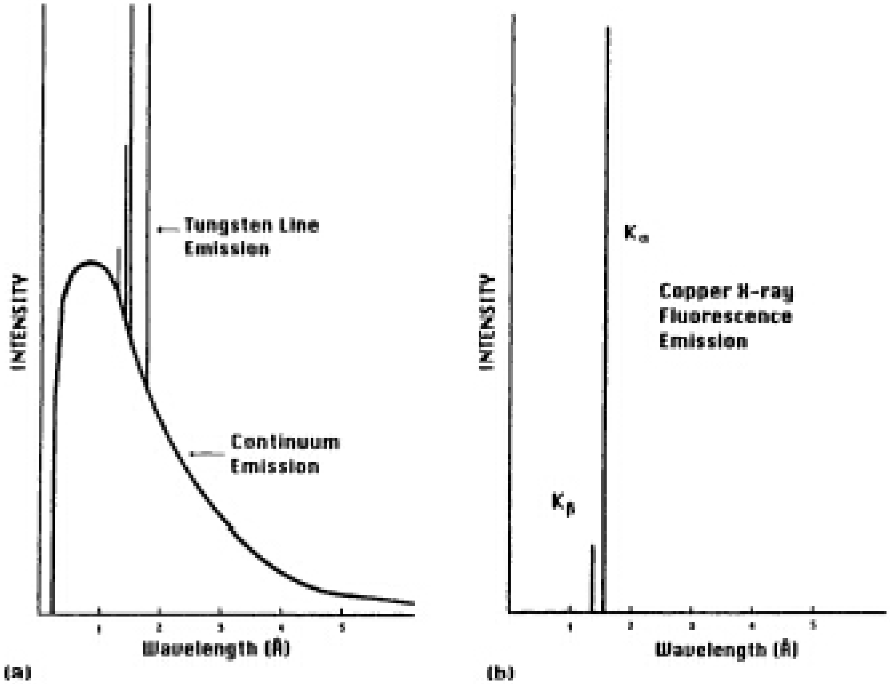

Figure 8.13 (a) The primary X-ray emission from a tungsten target. (b) The secondary emission from a copper target. Note the removal of the continuum radiation and the nearly monochromatic output from the secondary target. (From Parsons, used with permission.)

and the intensity of the source drops off with time, depending on the half-life of the isotope. 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.

8.2.2. Collimators

The X-rays emitted by the anode are radially directed. As a result, they form a hemisphere with the target at the center. In WDXRF spectroscopy or XRD structural determination, the monochromator's analyzing crystal or the crystalline substance undergoing structure determination requires a nearly parallel beam of radiation to function properly. A narrow, nearly parallel beam of X-rays can be made by using two sets of closely packed metal plates separated by a small gap. This arrangement absorbs all the radiation except the narrow beam that passes between the gap. Decreasing the distance between the plates or increasing the total length of the gap decreases the divergence of the beam of X-rays (i.e., it collimates, or renders them parallel). The use of a collimator increases the wavelength resolution of a monochromator's analyzing crystal, cuts down on stray X-ray emission, and reduces background. Commercial instruments use multiple tube or multiple slit collimator arrangements, often both before the analyzing crystal (the primary collimator) and before the detector (the secondary collimator). The collimator positions in a sequential WDXRF spectrometer are shown schematically in Fig. 8.14. In many wavelength dispersive instruments, two detectors are used in tandem, and a third auxiliary collimator may be required. Such an arrangement is shown in Fig. 8.15.

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	Electron capture	2.7	5.9, 6.4 keV Mn K X-rays	28.5	5–100
^{109}Cd	Electron capture	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	Electron capture	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 et al., used with permission.

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

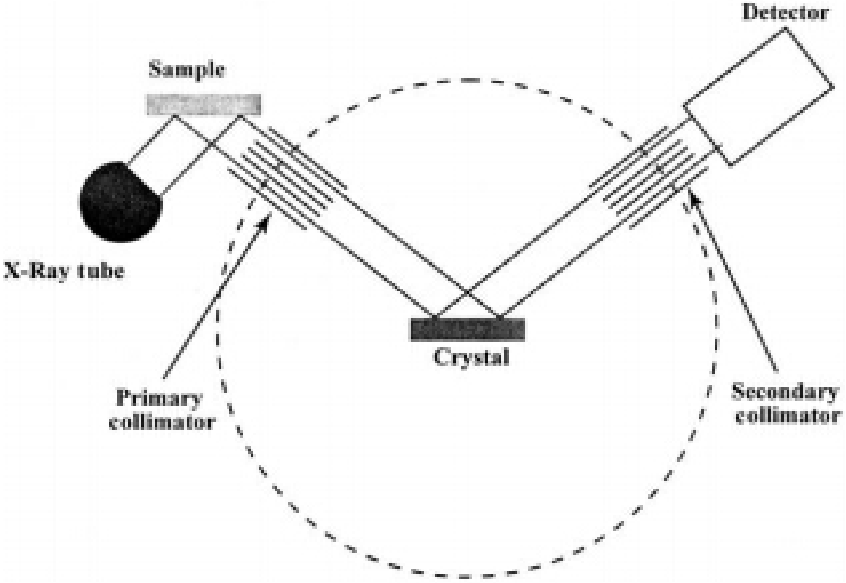

Figure 8.14 Schematic of the optical path in a wavelength-dispersive sequential spectrometer, showing the positions of the collimators. [Courtesy of PANalytical, Inc., The Netherlands (www.panalytical.com).]