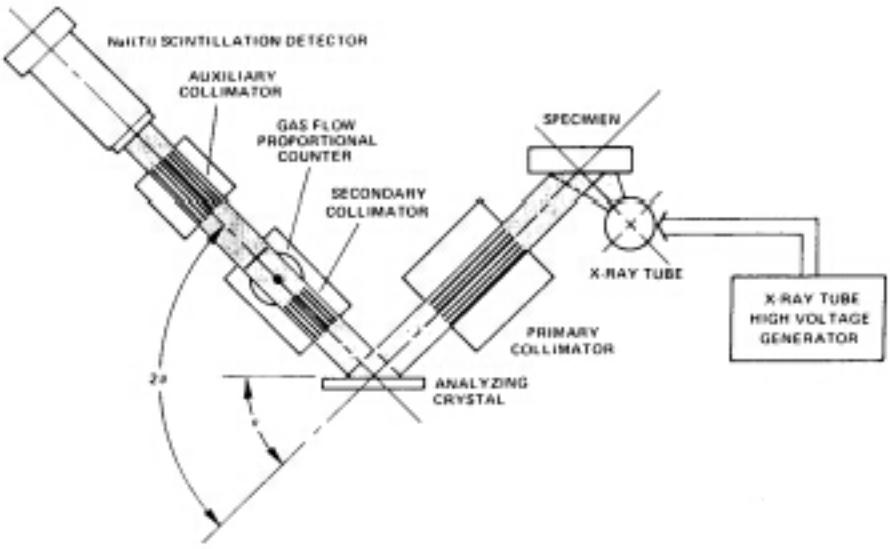

Figure 8.15 A sequential spectrometer with two tandem dectors, showing the placement of the collimators in the optical path. (From Jenkins et al., 1981, used with permission.)

Collimators are not needed for curved crystal spectrometers where slits or pinholes are used instead nor are they needed for energy dispersive spectrometers.

8.2.3. Filters

One of the problems of using the X-ray tube illustrated in Fig. 8.9 is that both continuum and characteristic line radiation is generated at certain operating voltages, as seen in Fig. 8.3. For many analytical uses, only one type of radiation is desired. Filters of various materials can be used to absorb unwanted radiation but permit radiation of the desired wavelength to pass by placing the filter between the X-ray source and the sample.

A simple example of how a filter is used is shown in Fig. 8.16. The solid line spectrum is the output of a Rh tube operated at 20 kV with no filter between the tube and the detector. The Rh L_α line at 2.69 keV is seen, along with a broad continuum of X-rays from 4 to 19 keV. If the Rh L_α line gets scattered into the detector, as it can from a crystalline sample, it can be mistaken for an element in the sample or may overlap another line, causing spectral interference. Placing a cellulose filter over the tube window causes the low energy Rh characteristic line to be absorbed; only the continuum radiation reaches the detector, as shown by the dotted line spectrum.

Alternatively, when monochromatic radiation is desired, a filter is chosen with its absorption edge between the K_α and the K_β emission lines of the target element. The filter then absorbs the K_β line and all shorter wavelengths, including much of the continuum; the light reaching the sample is essentially the K_α line of the target. Filters are commonly thin metal foils, usually pure elements, but some alloys such as brass and materials like cellulose are used. Varying the foil thickness of a filter is used to optimize peak-to-background ratios. Commonly used filters for various targets are listed in Table 8.5. Figure 8.17 shows a commercial sequential X-ray spectrometer with a series of selectable beam filters located between the X-ray tube and the sample. The filters are computer-controlled and are changed automatically according to the analytical program set up in the instrument software.

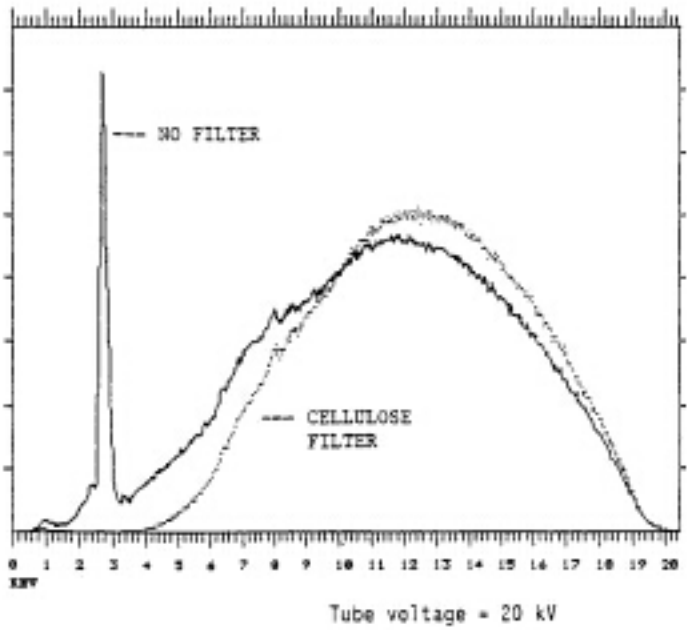

Figure 8.16 The use of a filter to remove unwanted radiation from entering the spectrometer is demonstrated. A cellulose filter placed between a Rh X-ray tube and the sample removes the Rh L_α line at 2.69 keV and allows only the continuum radiation to excite the sample. [Courtesy of ThermoNoran (www.thermo.com).]

8.2.4. WDXRF Spectrometers

Schematics of sequential WDXRF spectrometers are shown in Figs. 8.14, 8.15, and 8.17. In the configurations shown, the source is placed under the sample; the sample is presented surface-down to the X-ray beam. Some instruments have the tube above the sample, with the sample surface facing up. There are advantages and disadvantages to both designs, as we shall see. The sample fluoresces as a result of excitation by the source. The sample fluorescence is directed through the primary collimator to the *analyzing crystal*. Diffraction

Table 8.5 Filters for Commonly Available X-Ray Tubes

Target	Target K_α (Å)	Target K_β (Å)	Filter element	Filter K-edge (Å)	Foil thickness (μm)	% K_β absorbed
Cr	2.289	2.085	V	2.269	15.3	99.0
Fe	1.936	1.757	Mn	1.896	12.1	98.7
Co	1.789	1.621	Fe	1.743	14.7	98.9
Ni	1.658	1.500	Co	1.608	14.3	98.4
Cu	1.541	1.393	Ni	1.488	15.8	97.9
Mo	0.709	0.632	Zr	0.689	63.0	96.3
Ag	0.559	0.497	Pd	0.509	41.3	94.6
W	0.209	0.185				

Note: No suitable filter is available for tungsten.
Source: From Parsons, used with permission.

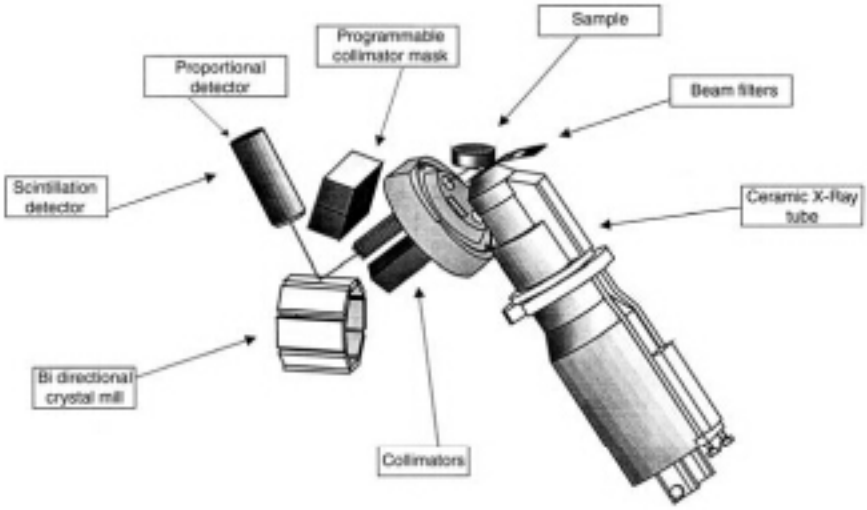

Figure 8.17 The schematic layout of a commercial sequential X-ray spectrometer, the MagiX, showing a series of selectable beam filters located between the X-ray tube and the sample. [Courtesy of PANalytical, Inc., The Netherlands (www.panalytical.com).]

occurs at the crystal planes according to Bragg's Law and X-rays of different wavelengths are diffracted at different angles. The diffracted X-rays are passed through another collimator to one or more detectors. Figure 8.15 depicts two detectors in tandem, one behind the other. The analyzing crystal is mounted on a turntable that can be rotated through θ degrees (see the arrow marked θ on the lower left side of the diagram). The detector(s) are connected to the crystal turntable so that when the analyzing crystal rotates by θ degrees, the detector rotates through 2θ degrees, as shown by the marked arrow. Therefore the detector is always in the correct position (at the Bragg angle) to detect the dispersed and diffracted fluorescence. This crystal positioning system is called a **goniometer**. Figure 8.18 shows the turntable and the concentric circles made by the crystal and the detector. In most systems, the maximum diffraction angle attainable is 75° θ (or 150° 2θ).

In some systems the rotation of the crystal and the detector is mechanically coupled with gears. Other systems have no mechanical coupling but use computer-controlled stepper motors for the crystal and the detector. The newest systems use optical position control by optical sensors or optical encoding devices. Optical position control permits very high angular precision and accuracy and very fast scanning speeds.

8.2.4.1. The Analyzing Crystal

As we have discussed, a crystal is made up of layers of ions, atoms, or molecules arranged in a well-ordered system, or lattice. If the spacing between the layers 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 (Fig. 8.8). Bragg's Law [Eq. (8.14)] indicates 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. If an X-ray beam consisting of a range of wavelengths falls on the crystal, the diffracted beams of different wavelengths emerge at different angles. The incident beam is thus split up by the crystal into its component X-ray wavelengths, just as a prism or grating splits up white light into a spectrum of its component colors. The principle is illustrated

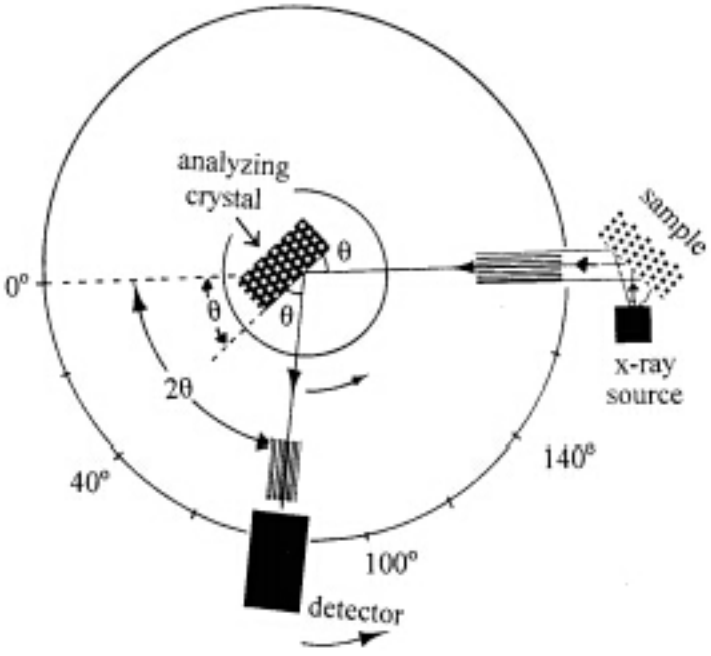

Figure 8.18 Goniometer layout for a sequential XRF spectrometer.

in Fig. 8.19. Figure 8.19 shows schematically that two detectors placed at the proper locations could detect the two wavelengths simultaneously. Alternatively, the detector or analyzing crystal could move, allowing each wavelength to be detected sequentially. Both types of spectrometers are commercially available. Some crystals in common use for dispersion of X-rays in commercial XRF spectrometers are listed in Table 8.6.

The analyzing crystal is an X-ray monochromator. The crystal separates X-rays of different wavelengths by diffracting them at different angles. Bragg's Law fixes the spectral range of a given crystal. Since the maximum value of $\sin\theta$ is 1.00, the upper spectral limit $\lambda_{max} = 2d$. The diffraction efficiency and the resolution depend on the purity and perfection of the crystal lattice. The crystal should be as perfect as possible, so that the d spacing for a given plane will be constant in all parts of the crystal. As is clear from Table 8.6, different crystals are needed to measure different elements. Commercial sequential XRF systems have a computer-controlled multiple crystal holder inside the spectrometer, with positions for as many as 8–10 crystals in some instruments. The crystals are interchanged but the same goniometer is used to select the diffraction angle, meaning that only one wavelength can be measured at a time with a sequential system.

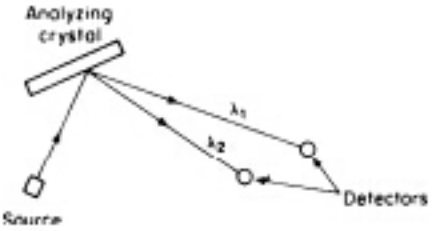

Figure 8.19 The analyzing crystal as a monochromator.

Table 8.6 Crystals Used for X-Ray Monochromators

Crystal	Orientation (Miller indices)	2*d* (Å)	Useful element range (atomic number)	Remarks
Lithium fluoride	420	1.80	Ni (28)–U (92)	High resolution
	220	2.85	V (23)–U (92)	High resolution, good intensity
	200	4.02	K (19)–U (92)	General purpose, highest intensity
Silicon	111	6.26	K (19), S (16), Cl (17)	
Germanium	111	6.53	K (19), S (16), Cl (17)	Good for low and intermediate Z elements
Pyrolytic graphite	002	6.71	K (19), S (16), Cl (17)	Good intensity, poor resolution
Indium antimonide	111	7.84	Si (14)	
Pentaerythritol	002	8.72	Al (13)–Cl (17)	Good intensity, soft
Thallium hydrogen phosphate (TlAP)	100	5.75	O (8)–Mg (12)	Poisonous
Synthetic Multilayers[a]				
PX-1		51	O (8)–Mg (12)	Low resolution, good intensity
PX-3		195	B (5)	Low resolution, good intensity
PX-4		122	C (6), N (7), O (8)	Low resolution, good intensity
OVO 55		55	Mg (12), Na (11), F (9)	Low resolution, good intensity
OVO H300		300	Be (4), B (5)	One of the largest spacings available

Source: Data from Helsen and Kuczumow, used with permission.
[a]The designations listed for these synthetic multilayers are commercial tradenames from different instrument manufacturers. A more generic approach is to classify them according to their *d* spacing.

A serious limitation in XRF was the lack of natural crystals with *d* spacings large enough to diffract the low energy X-rays from low atomic number elements. That limitation has been overcome by the synthesis of multilayer "pseudocrystals". These are made from alternating layers of materials with high and low optical densities deposited on a silicon or quartz flat. The PX3 multilayer is made from B_4C alternating with Mo, for example. These engineered multilayers are stable, commercially available, and permit the routine determination of elements as light as Be in samples.

The analyzing crystal shown schematically in Fig. 8.14 has a flat surface. Flat crystals are used in scanning (sequential) spectrometers. Curved crystals, both natural and synthetic multilayers, are used in simultaneous spectrometers, electron microprobes, and for synchrotron X-ray spectrometry. The advantage to a curved crystal is that the X-rays are focused and the collimators replaced by slits, resulting in much higher intensities than with flat crystal geometry. This makes curved crystals excellent for analysis of very small samples. The use of a curved crystal and slits in a simultaneous spectrometer is illustrated schematically