8.2.3 Instrumentation for Wavelength-Dispersive X-Ray Spectrometry

Instruments:

There are three types of WDXRF instruments: **sequential spectrometers**, which use a goniometer and sequentially measure the elements by scanning the wavelength; **simultaneous spectrometers**, which use multiple channels, with each channel having its own crystal/detector combination optimized for a specific element or background measurement; and **hybrid spectrometers**, which combine sequential goniometers or scanners with fixed channels as well as XRD channels and goniometers. Hybrid instruments will be discussed in Section 8.4 with XRD instruments.

Components: A WDXRF spectrometer can be generally divided into four major components based on their functionality: the generator, spectrometer, electronic pulse processing unit, and sample changer. The **generator** supplies the current and high voltage for the X-ray tube to produce the tube radiation (primary X-rays). The generators available today can provide a maximum output of around 4 kW with a maximum voltage of up to 70 kV and up to 170 mA current. *2. spectrometer:*

The **spectrometer** contains the X-ray tube, primary beam filters, collimators, analyzing crystals, and detectors. Parts of the spectrometer and the sample measurement position are generally under vacuum, but other atmospheres (purge gases) can be used based on the desired application. X-ray tubes and primary beam filters have been discussed earlier. Most commercially available WDXRF units today use end-window X-ray tubes, which are water-cooled. The window thickness is around 75 µm or less (see Figure 8.10). *Beam filters*

The primary beam filter wheel is equipped with a selection of absorbing foils, commonly Al and Cu foils of various thicknesses. It is located between the tube and the sample, filtering out undesirable or interfering components of the tube radiation to increase the peak-to-background ratio.

8.2.3.1 Collimators

The X-rays emitted by the anode in an X-ray tube are radially directed. As a result, they form a hemisphere with the target at the center. In WDXRF spectroscopy or XRD structural determination, the spectrometer'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 or blades separated by small gaps. This arrangement absorbs all the radiation except the narrow beam that passes between the gaps (Figure 8.28).
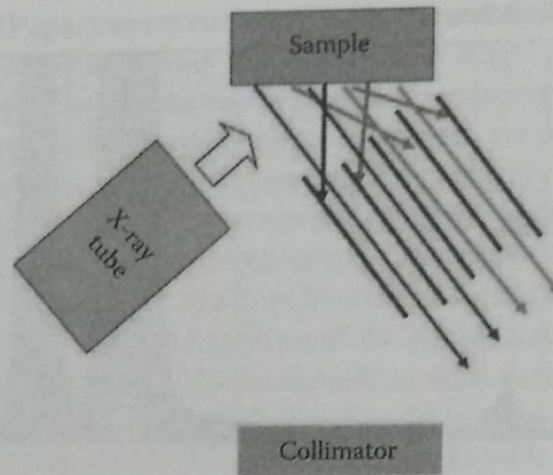
Figure 8.28 The function of a collimator is shown. All radiation is absorbed except for the photons passing through the gaps, forming a narrow, nearly parallel beam of X-rays. (© 2013 Bruker, Inc. www. bruker.com. Used with permission.)

Function of collimators:

Decreasing the distance between the plates or increasing the total length of the gaps 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 spectrometer's analyzing crystal, cuts down on stray X-ray emission, and reduces background (Figure 8.29). *multiple slit collimator:*

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 Figure 8.30. In many wavelength-dispersive (WD) instruments, two detectors are used in tandem, and a third auxiliary collimator may be required. Such an arrangement is shown in Figure 8.31.

Collimators are not needed for curved crystal spectrometers where slits or pinholes are used instead nor are they needed for ED spectrometers. **Collimator masks** are situated between the
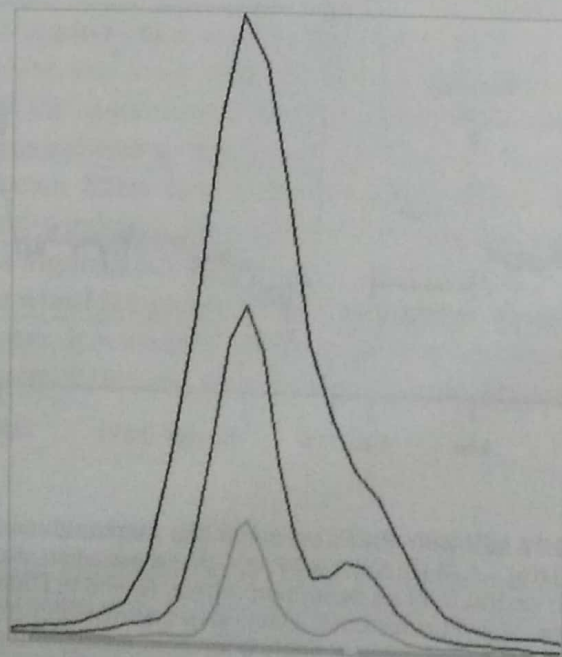

Figure 8.29 Peak resolution and intensity as a function of finer and finer divergence (blade spacing). Finer divergence increases resolution but decreases intensity. (© 2013 Bruker, Inc. www. bruker.com. Used with permission.)
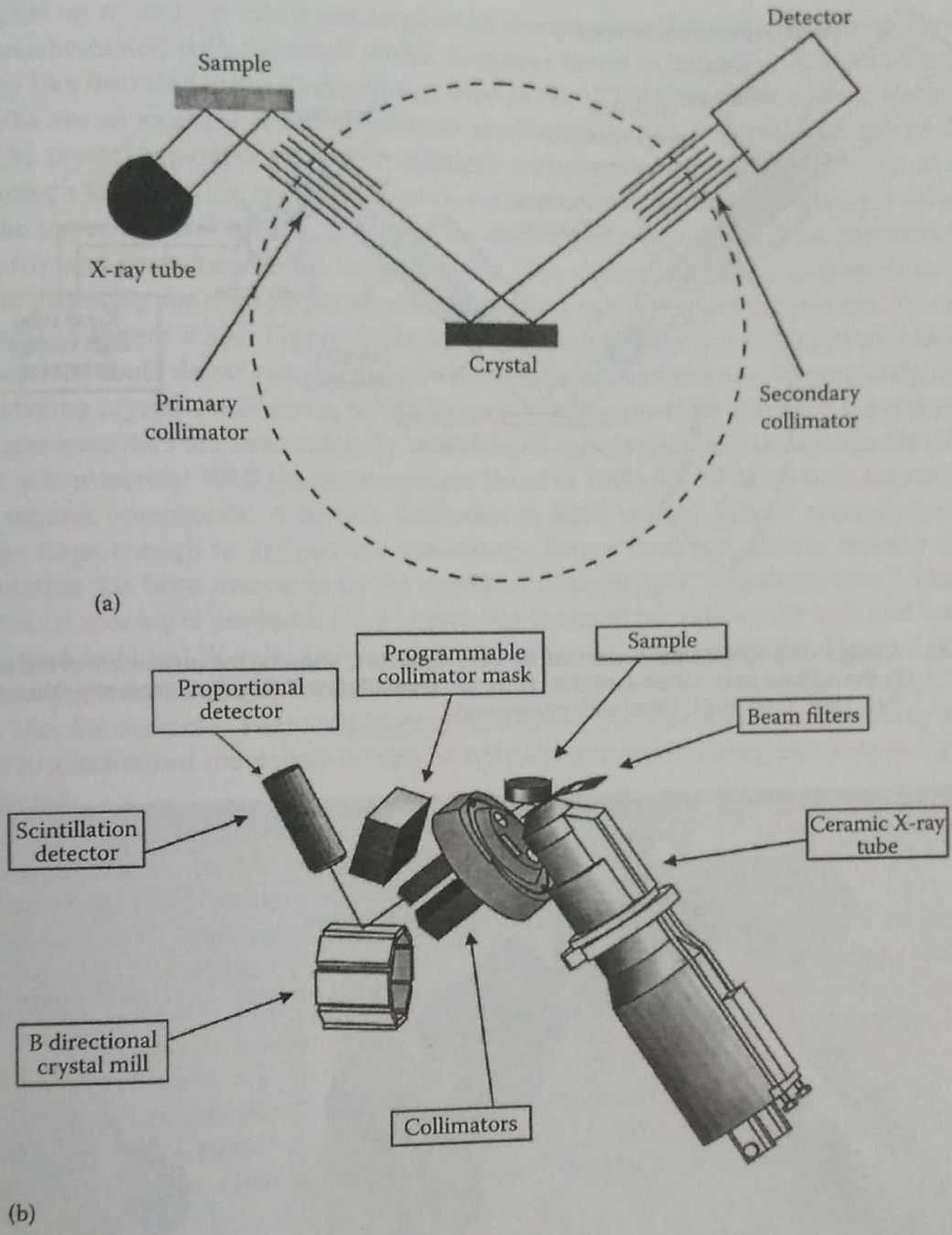
(a)

(b)

Figure 8.30 (a) Schematic of the optical path in a WD sequential spectrometer, showing the positions of the collimators. (b) Schematic layout of a commercial sequential WDXRF system. (Courtesy of PANalytical, Inc., The Netherlands. www.panalytical.com.)

sample and collimator and serve the purpose of cutting out the radiation coming from the edge of sample cup aperture (Figure 8.32).

8.2.3.2 Analyzing Crystals

The analyzing crystals are the "heart" of a WDXRF spectrometer. 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 (Figure 8.8).
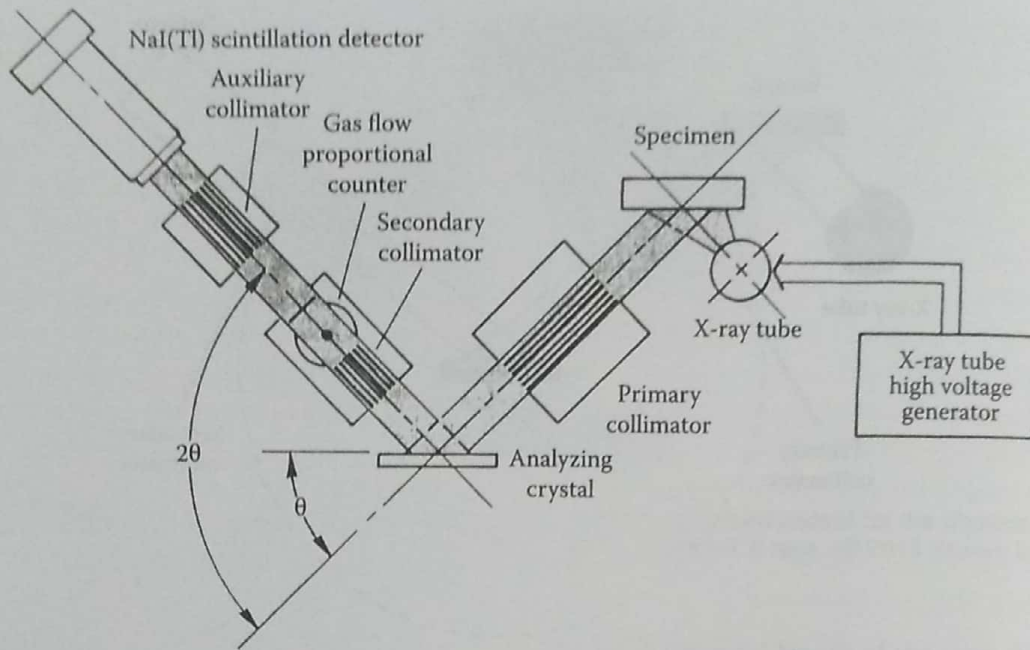
Figure 8.31 A sequential spectrometer with two tandem detectors, showing the placement of the collimators in the optical path. (From Jenkins, R. et al., *Quantitative X-Ray Spectrometry*, Marcel Dekker, Inc., New York, 1981. Used with permission.)
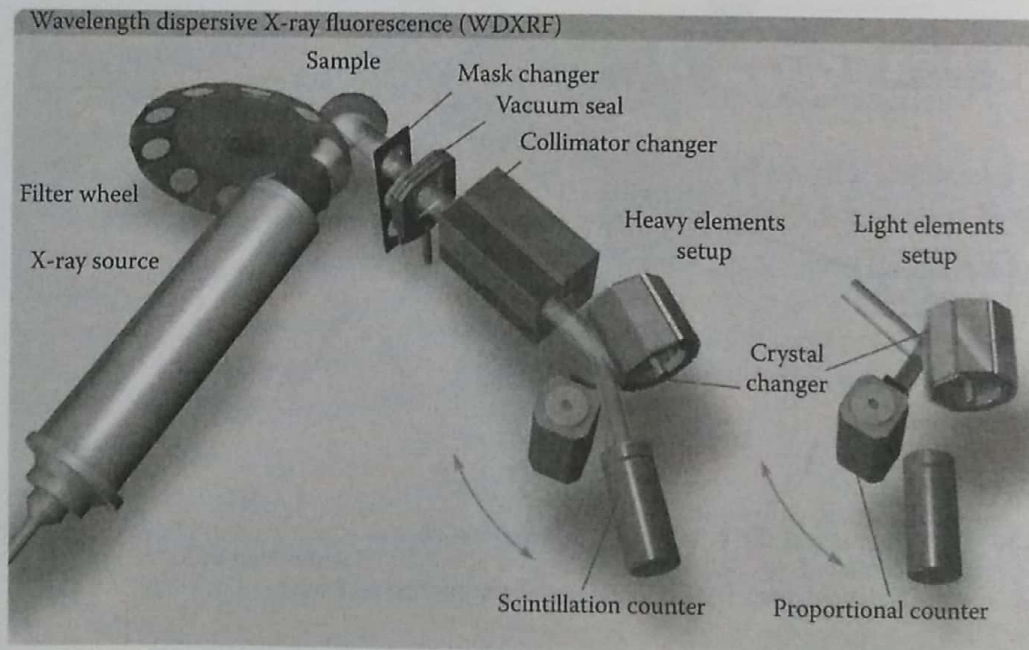

Figure 8.32 Schematic commercial WDXRF system showing the position of a collimator mask changer, as well as the layout of X-ray tube, filter wheel, sample, collimator, analyzing crystal changer, and detector. (© 2013 Bruker, Inc. www.bruker.com. Used with permission.)

Bragg's Law (Equation 8.15) 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 analyzing crystal is an X-ray monochromator, with the small lattice distances found in natural or synthetic crystals acting exactly like the ruled diffraction gratings used in the UV/visible (VIS) region. Because X-ray wavelengths are so small, it is not possible to mechanically rule a grating for use in the X-ray region. 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. The principle is illustrated in Figure 8.33a. Figure 8.33a shows schematically that two detectors placed at the proper locations could detect two diffracted 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 8.7. Most crystals are natural inorganic or organic compounds. 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." The desired lattice plane d-spacing is produced from alternating layers of materials with high and low optical densities, such as Si and W or Ni and BN, deposited on a silicon or quartz flat. Figure 8.33b shows how such a synthetic multilayer crystal functions. The PX-3 multilayer is made from B_4C alternating with Mo, for example. These engineered multilayers are stable and commercially available and have revolutionized the determination of light elements, permitting elements as light as Be to be detected.

When applying Bragg's law, the d-spacing of a specific analyzing crystal limits its detectable element range. The shorter the d-spacing of a crystal, the better the separation of two adjacent or overlapping peaks. For example, looking at vanadium (V) and chromium (Cr), the V K_{α_1} and Cr K_{α_1} lines are farther apart when measured with LiF-220 ($2d = 0.2848$ nm) than when measured with LiF-200 crystal ($2d = 0.4028$).

As is clear from Table 8.7, 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, as seen in Figure 8.32.

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 Figure 8.31). The detector(s) are connected to the crystal turntable so that when the analyzing crystal rotates by θ degrees, the detector rotates
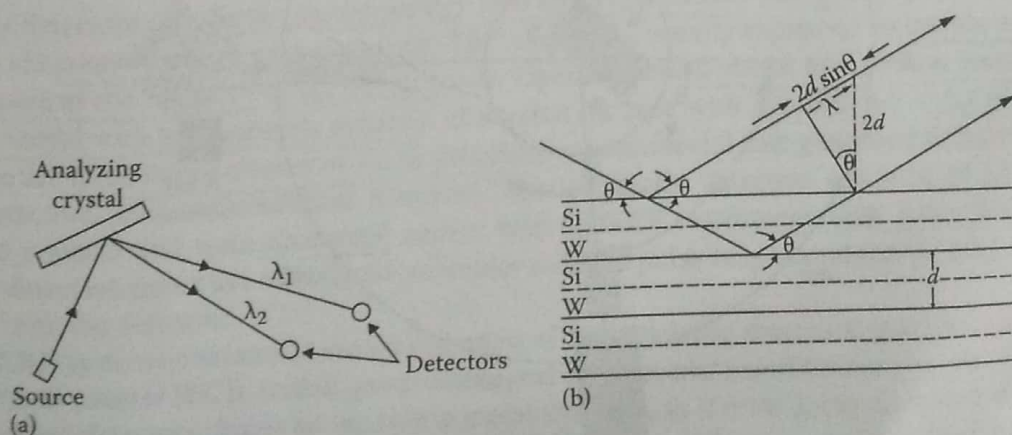

Figure 8.33 (a) The analyzing crystal as a monochromator. (b) A synthetic crystal made from multiple alternating layers of Si and W, showing the d-spacing and the ability to diffract X-rays. (b: © 2013 Bruker, Inc., www.bruker.com. Used with permission.)

Table 8.7   Analyzing Crystals Used in Modern X-Ray Spectrometers

Crystal	Name and Orientation (Miller Indices)	2d-Spacing (nm)	Element Range
LiF-420	Lithium fluoride (420)	0.1891	$\geq NiK_{\alpha_1}$
LiF-220	Lithium fluoride (220)	0.2848	$\geq VK_{\alpha_1}$
LiF-200	Lithium fluoride (200)	0.4028	$\geq KK_{\alpha_1}$
Ge	Germanium (111)	0.6530	P, S, Cl
InSb	Indium antimonide (111)	0.7481	Si
PET[a]	Pentaerythritol (002)	0.8740	Al–Ti, Kr–Xe, Hf–Bi
ADP	Ammonium dihydrogen phosphate	1.064	Mg
TlAP[b]	Thallium acid phthalate (100) (Thallium hydrogen phthalate)	2.576	Fe–Na
XS55, OV055, AX06, PX-1, PX-3, and others	Multilayered synthetic crystal[c]	5.0–19	Light elements from Be to N, N–Al, Ca–Br depending on the d-spacing

[a] The most heat-sensitive crystal.
[b] Toxic.
[c] The designations for these multilayered synthetic crystals are commercial trade names from different instrument manufacturers.

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 8.34 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
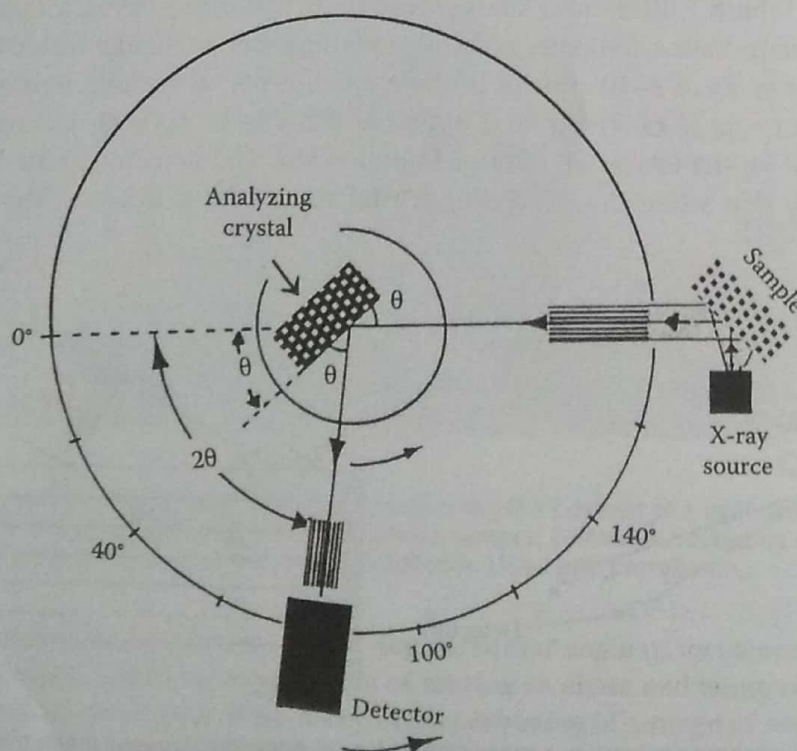

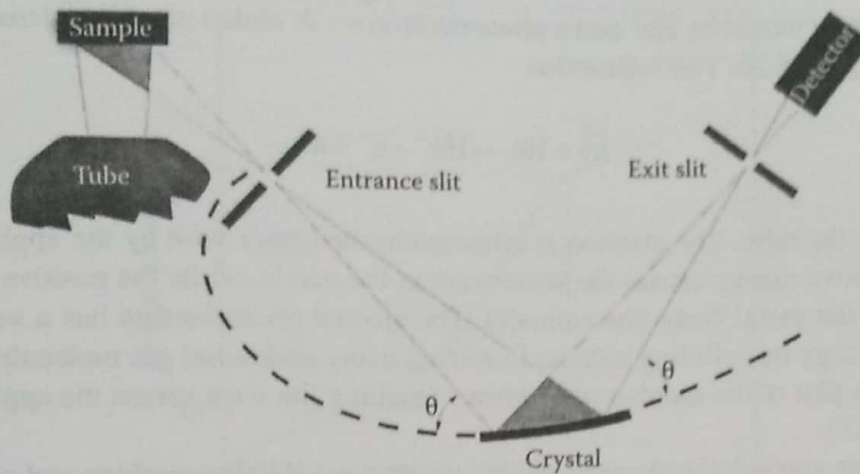**Figure 8.34**   Goniometer layout for a sequential XRF spectrometer.

Figure 8.35 Schematic of the optical path in a curved crystal spectrometer. (Courtesy of PANalytical, Inc., The Netherlands. www.panalytical.com.)

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.

The analyzing crystals are interchanged by rotation of the crystal holder, 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.

The analyzing crystal(s) shown schematically in Figures 8.30 through 8.32 have 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 at the detector 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 in Figure 8.35. The curved crystal spectrometer geometry should remind you of the Rowland circle geometry for optical emission spectrometers discussed in Chapter 7. Curved crystals are used in the "fixed" channel design of most simultaneous (multichannel) spectrometers.

8.2.3.3 Detectors

X-ray detectors transform photon energy into electrical pulses. The pulses (and therefore, the photons) are counted over a period of time. The *count rate*, usually expressed as counts per second, is a measure of the intensity of the X-ray beam. Operating the detector as a photon counter is particularly useful with low-intensity sources, as is often the case with X-radiation. *classes:*

There are three major classes of X-ray detectors in commercial use: gas-filled detectors, scintillation detectors, and semiconductor detectors. Semiconductor detectors are used in EDXRF and handheld systems and were discussed earlier with EDXRF instrumentation. Both WDXRF and EDXRF detection make use of a signal processor called a pulse height analyzer or selector in conjunction with the detector.

WDXRF systems commonly use one or more of the following detectors: gas flow proportional counter (flow counter [FC]), sealed gas-proportional counter, and scintillation counters (SC).

Gas-filled detectors. Suppose we take a metal cylinder, fit it with X-ray transparent windows, place in its center a positively charged wire, fill it with inert filler gas, such as helium, argon, or xenon, and seal it. If an X-ray photon enters the cylinder, it will collide with and ionize a molecule of the filler gas by ejecting an *outer shell electron*, creating a *primary ion pair*. With helium as a

filler gas, the ion pair would be He⁺ and a photoelectron e⁻. A sealed gas-filled detector of this type is illustrated in Figure 8.36. The interaction

$$hv + He \rightarrow He^+ + e^- + hv$$
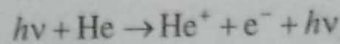
takes place inside the tube. The electron is attracted to the center wire by the applied potential on the wire. The positive charge causes the wire to act as the anode, while the positive ion, He⁺ in this case, migrates to the metal body (the cathode). The ejected photoelectron has a very high kinetic energy. It loses energy by colliding with and ionizing many additional gas molecules as it moves to the center wire. A plot of the number of electrons reaching the wire versus the applied potential is given in Figure 8.37.

With no voltage applied, the electron and the positive ion (He⁺) recombine and no current flows. As the voltage is slowly increased, an increasing number of electrons reach the anode, but not all of them; recombination still occurs. This is the sloping region marked A in Figure 8.37. At the plateau marked B in Figure 8.37, all the electrons released by a single photon reach the anode and the current is independent of small changes in the voltage. A detector operating under these voltage conditions is known as an *ionization counter*. Ionization counters are not used in X-ray spectrometers because of their lack of sensitivity.
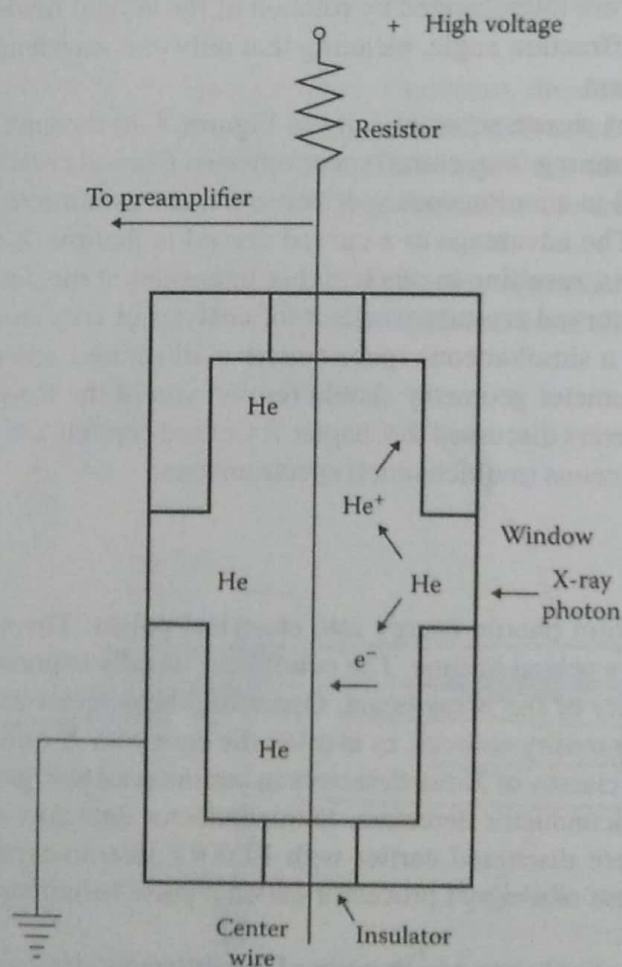

Figure 8.36 Schematic diagram of a gas-filled X-ray detector tube. He filler gas is ionized by X-ray photons to produce He⁺ ions and electrons, e⁻. The electrons move to the positively charged center wire and are detected. (Modified from Parsons, M.L., X-ray methods, in Ewing, G.W. (ed.), *Analytical Instrumentation Handbook*, 2nd edn., Marcel Dekker, Inc., New York, 1997. Used with permission.)
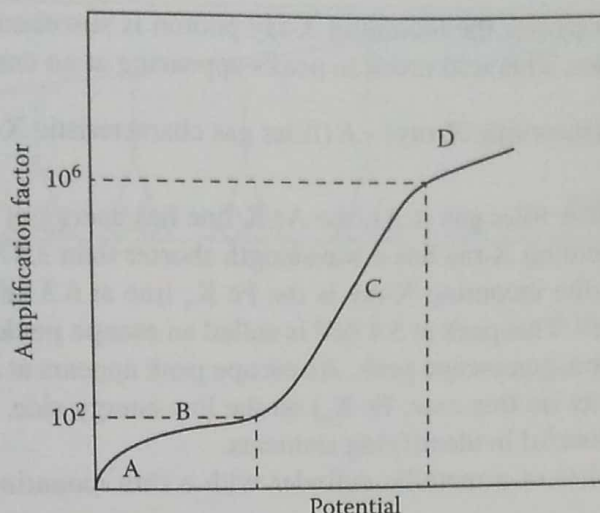
Figure 8.37 Gas-filled detector response versus potential. A detector operating at the plateau marked B is an ionization counter. A proportional counter operates in the sloping region marked C where the response is proportional to the energy of the incoming photon. The plateau marked D represents the response of a Geiger counter. (Modified from Helsen, L.A. and Kuczumow, A., 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.)

As the voltage increases further, the electrons moving toward the center wire are increasingly accelerated. More and more electrons reach the detector as a result of an avalanche of secondary ion pairs being formed, and the signal is greatly amplified. In the region marked C in Figure 8.37, the current pulse is proportional to the energy of the incoming X-ray photon. This is the basis of a *proportional counter*. In X-ray spectrometry, gas-filled detectors are used exclusively in this range, that is, as proportional counters. The amplification factor is a complex function that depends on the ionization potential of the filler gas, the anode potential, the mean free path of the photoelectrons, and other factors. It is critical that the applied potential, filler gas pressure, and other factors be kept constant to produce accurate pulse amplitude measurements. There are two main types of proportional counter: flow proportional counters and sealed proportional counters.

As shown in Figure 8.37, if the voltage is further increased, electrons formed in primary and secondary ion pairs are accelerated sufficiently to cause the formation of more ion pairs. This results in huge amplification in electrons reaching the center wire from each X-ray photon falling on the detector. The signal becomes independent of the energy of the photons and results in another plateau, marked D. This is called the Geiger–Müller plateau; a detector operated in this potential range is the basis of the *Geiger counter* or *Geiger–Müller* tube. It should be noted that a Geiger counter gives the highest signal for an X-ray beam without regard to the photon energy. However, it suffers from a long *dead time*. The dead time is the amount of time the detector does not respond to incoming X-rays. It occurs because the positive ions move more slowly than the electrons in the ionized gas, creating a *space charge*; this stops the flow of electrons until the positive ions have migrated to the tube walls. The dead time in a Geiger counter is on the order of 100 μs, about 1000 times longer than the dead time in a proportional counter. Due to the long dead time compared with other detectors, Geiger counters are not used for quantitative X-ray spectrometry. They are, however, very important portable detectors for indicating the presence or absence of X-rays. Portable radiation detectors equipped with Geiger counters are used to monitor the operation of equipment that creates or uses ionizing radiation to check for leaks in the shielding.

As was the case with EDXRF, escape peaks that are detector artifacts occur in WDXRF gas-filled detectors. Ionization of the filler gas by an X-ray photon usually results in the ejection of an outer shell electron. However, it is possible for ionization to occur by ejection of an inner

shell electron. When this happens, the incoming X-ray photon is absorbed, and the filler gas emits its characteristic K or L lines. This will result in peaks appearing at an energy E' equal to

$$E' = E \text{(incoming X-ray)} - E \text{(filler gas characteristic X-ray)} \qquad (8.18)$$

As an example, if the detector filler gas is Ar, the Ar K line has energy of about 3 keV (or a wavelength of 3.87 Å). If an incoming X-ray has a wavelength shorter than 3.87 Å, it can eject an argon K electron. Assuming that the incoming X-ray is the Fe K_α line at 6.3 keV, a peak will appear at $(6.4 - 3)$ keV or about 3.4 keV. This peak at 3.4 keV is called an **escape peak** and can be called either the Fe K_α escape peak or the argon escape peak. An escape peak appears at a constant distance from the parent fluorescence X-ray (in this case, Fe K_α) on the low-energy side. Escape peaks can often be very intense and can be useful in identifying elements.

FC. This detector consists of a metallic cylinder with a thin (counting) wire mounted in the middle (Figure 8.38).

The cylinder is filled with continuous flow of P-10 gas (10% methane [CH_4] and 90% Ar). A high positive voltage (+1400 to +1900 V) is applied to the thin wire. The cylinder is sealed with a
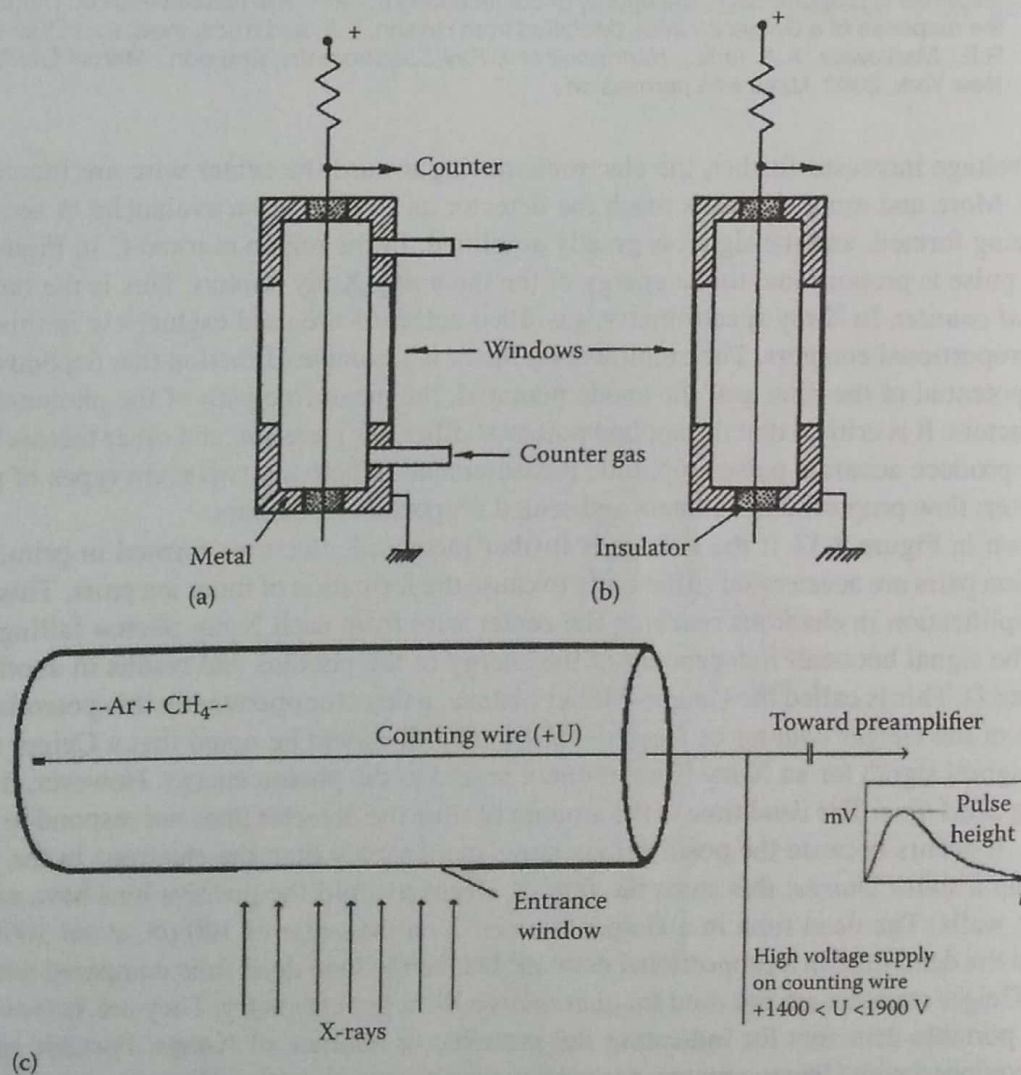

Figure 8.38 Schematics of (a) a flow proportional counter and (b) a sealed proportional counter. (From Helsen, L.A. and Kuczumow, A., in Van Griekin, R.E.; Markowicz, A.A. (eds.), *Handbook of X-Ray Spectrometry*, 2nd edn., Marcel Dekker, Inc., New York, 2002. Used with permission.) (c) Schematic view of a flow proportional counter.
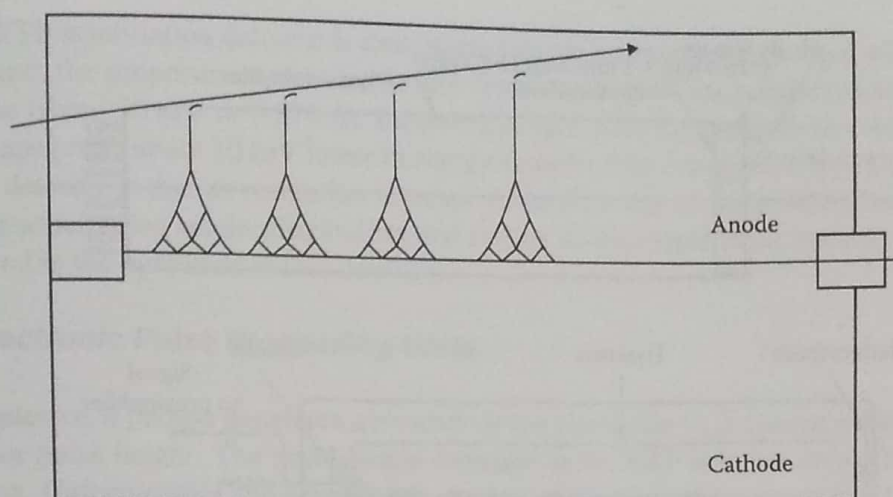
Figure 8.39 Four primary ions pairs produce four "avalanches," all of which contribute to a single pulse. (Copyright Oak Ridge Associated Universities, www.orau.org.)

0.3–1 μm very thin foil window permeable to X-ray photons with low energies and is thus suitable for measuring light elements, with Z < 27. The thin windows allow the filler gas to leak out; therefore, a supply of filler gas is constantly provided to the detector through the inlet as shown in Figure 8.38a. The pressure, flow, and temperature of the gas must be precisely controlled for accurate detector response.

X-ray photons interact with the inert gas in the detector by ionizing it. This ionization is based on the ejection of an outer shell electron and creates a primary ion pair. When argon is used, we will observe both an Ar^+ ion and an electron (e^-). The electron is attracted to the wire, which is positively charged, and the Ar^+ will be attracted and migrate to the metallic body. Each primary ion pair produces 10–10,000 electrons due to an "avalanche" of secondary pairs produced as the initial electrons are accelerated toward the wire (Figure 8.39). The principle of operation is that the number of electron–ion pairs created is proportional to the energy of X-rays that entered the detector. The pulse voltage as recorded by the counting electronics is proportional to the energy of the "counted" photon.

Sealed gas-proportional counter. This detector is a sealed or closed system with a fixed volume of filler gas (Figure 3.38b). The filler gas used in a sealed proportional counter may be Ne, Kr, or Xe. The detector is sealed with thicker windows than those used in the FC and therefore do not leak. Window materials include polymers, mica, aluminum, and beryllium. The window thickness generally prevents the sealed proportional counter from being used for the measurement of light elements from Be to Na. It is used for analyzing elements from Al to Ti.

Multiple proportional counters are used in simultaneous X-ray spectrometers, described later, while one proportional counter is often used in tandem with an SC in a sequential system. It is for this reason that the detector has two windows as shown in Figure 8.38. X-ray photons pass through the proportional counter to the SC located behind it, as illustrated in Figure 8.31, and signals are obtained from both detectors. It should be noted that this tandem arrangement does not permit independent optimization of both detectors. There are sequential spectrometer systems available with independent proportional and scintillation detectors.

SC. Photomultiplier detectors, discussed in Chapter 5, are very sensitive to visible and UV light, but not to X-rays, to which they are transparent. In a *scintillation detector*, the X-radiation falls on a compound that absorbs X-rays and emits visible light as a result. This phenomenon is called *scintillation*. A PMT can detect the visible light scintillations. The scintillating compound or phosphor can be an inorganic crystal, an organic crystal, or an organic compound dissolved in solvent.
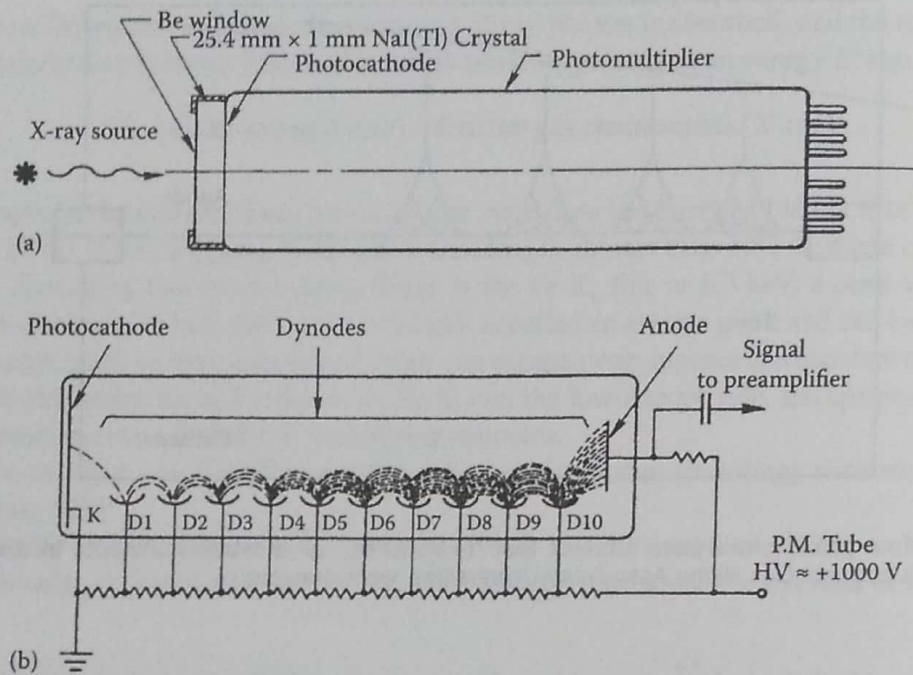
Figure 8.40 Schematic NaI(Tl) scintillation detector. (a) The assembled detector. (b) Schematic representation of the photomultiplier and its circuitry. (Courtesy of ORTEC (Ametek). www. ortec-online. com; From Jenkins, R. et al., *Quantitative X-Ray Spectrometry*, Marcel Dekker, Inc., New York, 1981. Used with permission.)

The most commonly used commercial scintillation detector has a thallium-doped sodium iodide crystal, NaI(Tl), as the scintillating material. A single crystal of NaI containing a small amount of homogeneously distributed Tl in the crystal lattice is coupled to a PMT, shown in Figure 8.40.

When an X-ray photon enters the crystal, it causes the interaction

$$I^- \rightarrow I^0 + e^-$$
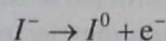
and the ejection of photoelectrons, as in the gas-filled detector. The ejected photoelectrons cause excited electronic states to form in the crystal by promotion of valence band electrons. When these excited electrons drop back to the ground state, flashes of visible light (scintillations) are emitted. The excited state lies about 3 eV above the ground state, so the emitted light has a wavelength of 410 nm. The intensity of the emitted light pulse from the crystal is proportional to the number of electrons excited by the X-ray photon. The number of electrons excited is proportional to the energy of the X-ray photon; therefore, the scintillation intensity is proportional to the energy of the X-ray.

The scintillations (visible light photons) from the crystal fall on the cathode of the PMT, which is made of a photoemissive material such as indium antimonide. Photoemissive materials release electrons when struck by photons. Electrons ejected from the cathode are accelerated to the first dynode, generating a larger number of electrons. The electron multiplication process occurs at each successive dynode, resulting in approximately 10^6 electrons reaching the anode for every electron that strikes the cathode. The amplitude of the current pulse from the photomultiplier is proportional to the energy of the X-ray photon causing the ionization in the crystal.

To summarize, the scintillation detector works by (1) formation of a photoelectron in the NaI(Tl) crystal after an X-ray photon hits the crystal, (2) emission of visible light photons from an excited state in the crystal, (3) production of photoelectrons from the cathode in the photomultiplier, and (4) electron multiplication.

The NaI(Tl) scintillation detector is most useful for short-wavelength X-rays, <2 Å (Z > 27), so it complements the proportional counter. It also has the potential for escape peaks caused by the iodine K line (about 30 keV or 0.374 Å). Incoming X-rays with wavelengths less than 0.374 Å will result in escape peaks about 30 keV lower in energy than the true energy. The major disadvantage of the NaI(Tl) detector is that its resolution is much worse than that of the proportional counter. This is due to the wider pulse height distribution that occurs in the output pulse because of the multiple steps involved in the operation of this detector.

8.2.3.4 Electronic Pulse Processing Units

In the detector, a photon generates a number of ion pairs, that is, a current pulse with a certain magnitude or pulse height. The pulse height (voltage) in an XRF detector depends on the energy of the photon. Unfortunately, the height of the current pulse that results is not exactly the same for photons of the same energy. Formation of ion pairs and secondary ion pairs is a statistically random process, so a Gaussian distribution of pulse heights centered on the most probable value results.

A series of pulses and their heights is shown in Figure 8.41. On the left side, this figure shows a series of current pulses from photons of two different energies counted over a period of time. If the pulses are plotted by height (amplitude), the result is a Gaussian **pulse height distribution**, shown on the right side of the figure. Two Gaussian pulse height distributions are seen since we had two photons of different energies reaching the detector. The width of the distribution is measured at half of the maximum height; this is called the FWHM. The FWHM is a measure of the energy resolution of a detector. Energy resolution is best in semiconductor detectors and worst in scintillation detectors, with gas-filled proportional counters in the middle.

In a WD instrument, the analyzing crystal separates the wavelengths falling on it, but as Bragg's law tells us, it is possible for higher-order (n > 1) lines of other elements to reach the detector. A higher-order line from a different element will have a very different energy and will result in a second pulse height distribution centered at a different energy reaching the detector. This would result in an error, since the signal would be misinterpreted as coming from just one element. This problem is eliminated by the use of a **pulse height discriminator**. The pulse height discriminator sets a lower and an upper pulse height threshold. Only the pulse heights that lie within these limits are counted. It thus reduces the background noise from the electronics and eliminates the interference of higher-order reflections. **A sine amplifier** ensures that a discriminator window, once set for a crystal, will be applicable for all detectable energies.
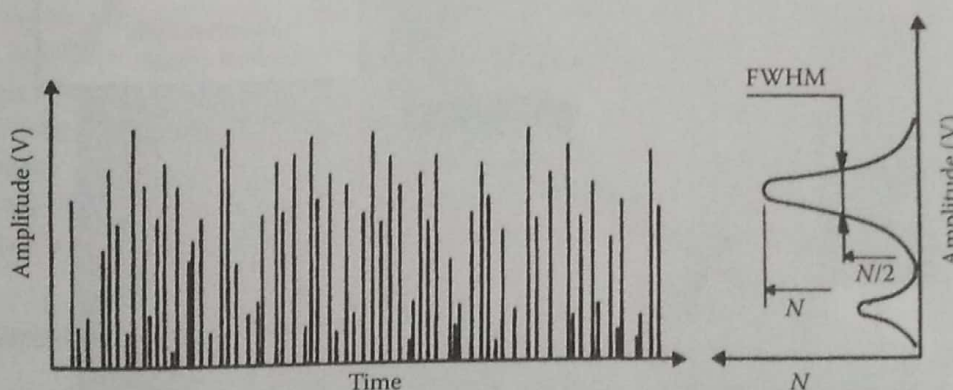

Figure 8.41 Amplitude or pulse height and time record of signals from the detector is on the left. Transformation of the data into a pulse height distribution is shown on the right. The FWHM measurement is shown for the higher peak. (From Helsen, L.A. and Kuczumow, A., in Van Griekin, R.E.; Markowicz, A.A. (eds.), *Handbook of X-Ray Spectrometry*, 2nd edn., Marcel Dekker, Inc., New York, 2002. Used with permission.)

Pulse processing also incorporates **dead time correction**. Dead time results from the inability of the detector electronics to process the pulses fast enough to match the volume of input signals. Therefore, the greater the incident intensity, the greater the losses would be during measurement. Dead time is typically 300–400 ns for modern spectrometers.

8.2.3.5 Sample Changers

Commercial instruments are equipped with automatic sample changers. These are of various types and sizes, permitting either controlled loading of samples with sequential access or X–Y random access.

8.2.4 Simultaneous WDXRF Spectrometers

A simultaneous WDXRF system, also called a multichannel system, uses multiple channels, optimized for a specific element or background measurement. Each individual channel consists of a crystal, detector, and electronics module and is dedicated to a specific wavelength. Instruments with as many as 38 fixed crystal/detector channels or as few as two are available. These systems are designed for specific applications, such as the analysis of steel in a production facility where hundreds of samples must be analyzed very quickly (e.g., in less than 60 s) for the same suite of elements every day.

It is difficult to arrange a large number of channels in close proximity to the sample. Therefore, curved crystal monochromators with slit optics are used (Figure 8.42). Two commonly used curvatures are those that follow a logarithmic spiral, shown in Figure 8.42, and the Johansson curvature, which results in a Rowland circle monochromator (Figure 8.43) with the curve of the crystal matching the curve of the Rowland circle. The curvature of the crystal is selected so that the X-ray entrance slit is focused by the crystal onto the exit slit. This allows for higher intensities in a space-saving geometric arrangement.

As seen in Figure 8.42, the X-ray beam is applied from above the sample in these systems. He detector is located behind the exit slit. Scintillation or gas-proportional counters are used depending
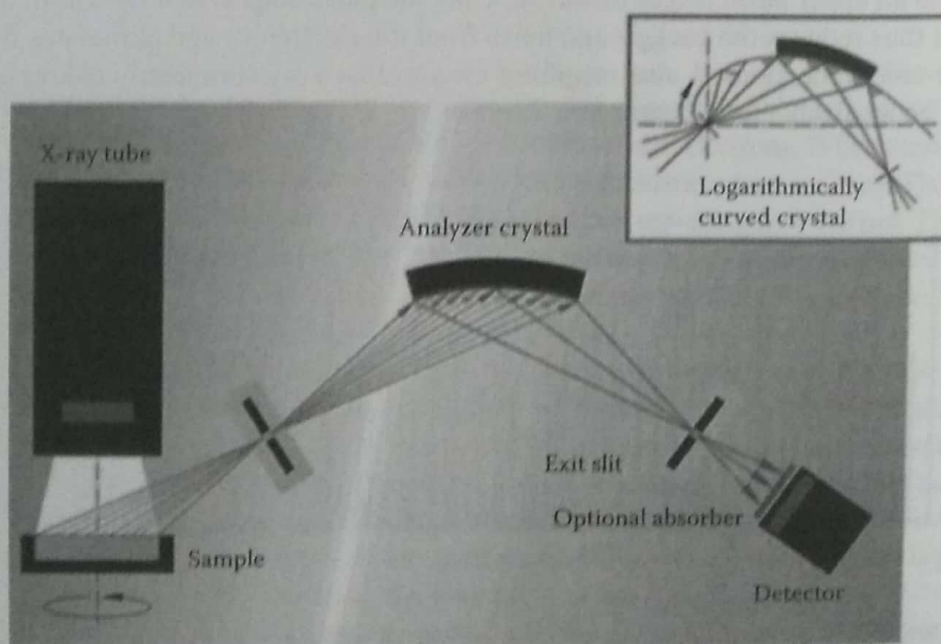

Figure 8.42 Monochromator schematic with a logarithmic spiral curved crystal. (© 2013 Bruker, Inc. www.bruker.com. Used with permission.)
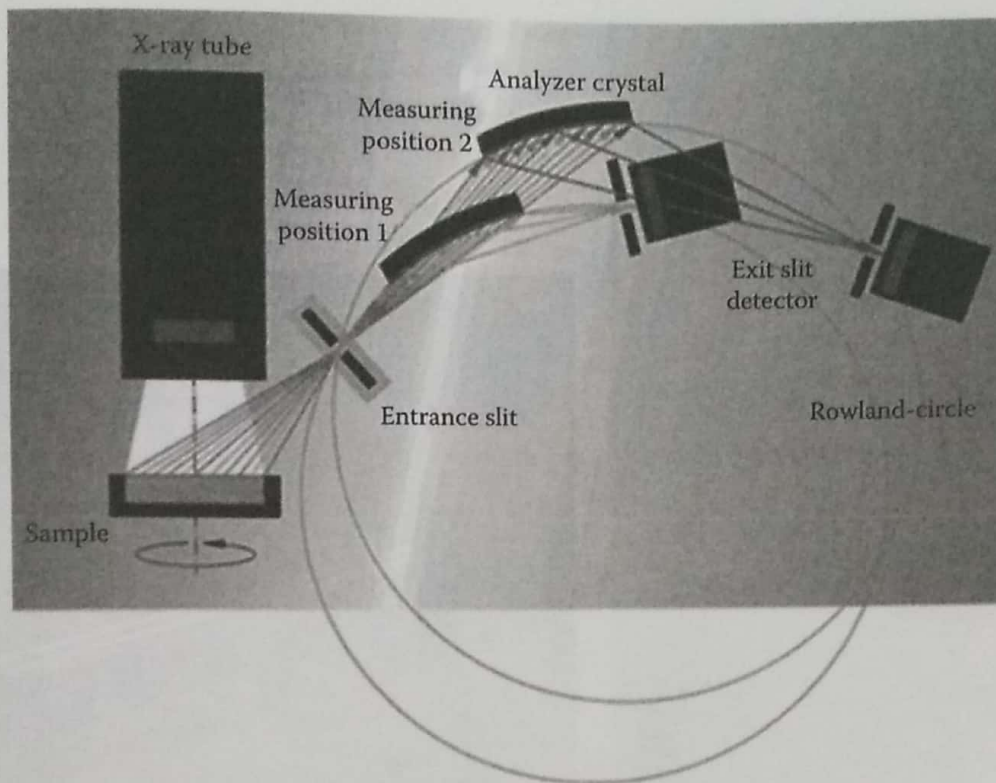
Figure 8.43 Rowland circle type monochromator schematic with a Johansson curved crystal used as a scanning channel. (© 2013 Bruker, Inc. www.bruker.com. Used with permission.)

on the wavelength. All the monochromators are located in a large vacuum chamber. All channels are measured simultaneously, so the generator setting must provide the best compromise for all of the elements measured. The measurement time depends on the statistical accuracy requirements of the element with the lowest intensity; the time is typically 20–60 s.

When measuring trace and major elements simultaneously, the generator is normally set so that the trace elements can be measured with the highest possible intensity. Absorbers or attenuators are then needed for the major element channels to reduce their intensities so that they are in the operational range of the detectors.

While the fixed channels are used exclusively for quantitative analysis, a scanner or movable channel may be installed in the vacuum chamber to provide qualitative analysis ability and some flexibility in what is otherwise a system with a fixed suite of elements.

A single crystal, usually LiF200 or pentaerythritol (PET), is used, and the scanner's 2θ angular range is limited to 30°–120°. Therefore, some elements must be measured in second order. The scanner works on the principle of the Rowland circle, in which the crystal and the detector move in such a way that the entrance slit, exit slit, and crystal lie on a fixed radius circle that changes in position, as shown in Figure 8.43. A typical commercial instrument is shown in Figure 8.44.