in Fig. 8.20. The curved crystal spectrometer geometry should remind you of the Rowland circle geometry for optical emission spectrometers discussed in Chapter 7.

8.2.4.2.   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.

There are three major classes of X-ray detectors in commercial use: gas-filled detectors, scintillation detectors, and semiconductor detectors. Semiconductor detectors will be discussed with EDXRF equipment. Both WDXRF and EDXRF detection makes use of a signal processor called a pulse height analyzer or selector in conjunction with the detector, and discussed subsequently.

8.2.4.3.   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 Fig. 8.21. The interaction

$$hv + He \longrightarrow He^+ + e^- + hv$$

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
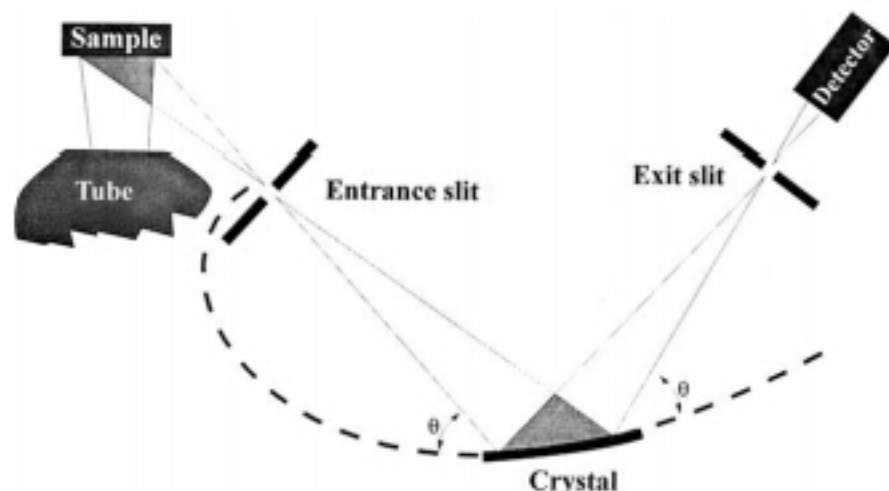
Figure 8.20 Schematic of the optical path in a curved crystal spectrometer. [Courtesy of PANalytical, Inc., The Netherlands (www.panalytical.com).]
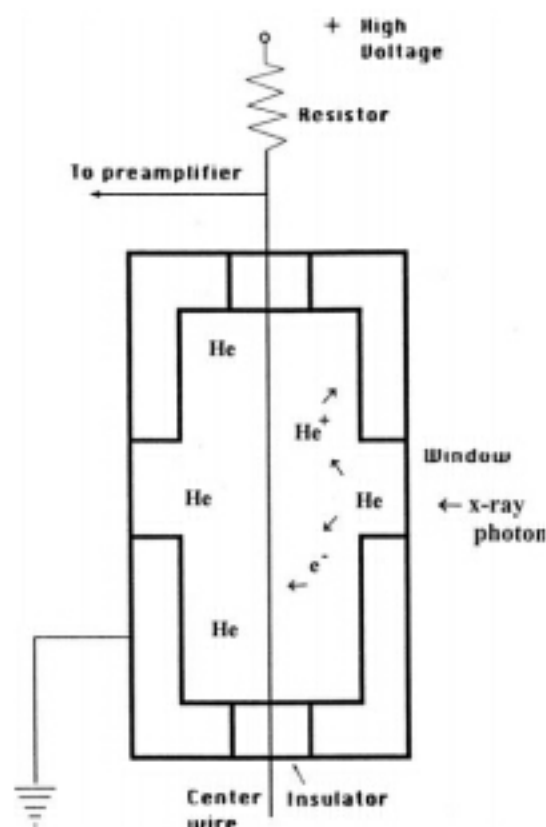
Figure 8.21   Schematic diagram of a gas-filled X-ray detector tube. He filler gas is ionized by X-ray photons to produce He^+ ions and electrons, e^-. The electrons move to the positively charged center wire and are detected. (Modified from Parsons, used with permission.)

additional gas molecules as it moves to the center wire. A plot of the number of electrons reaching the wire vs. the applied potential is given in Fig. 8.22.

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 Fig. 8.22. At the plateau marked B in Fig. 8.22, 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.

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 Fig. 8.22, 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
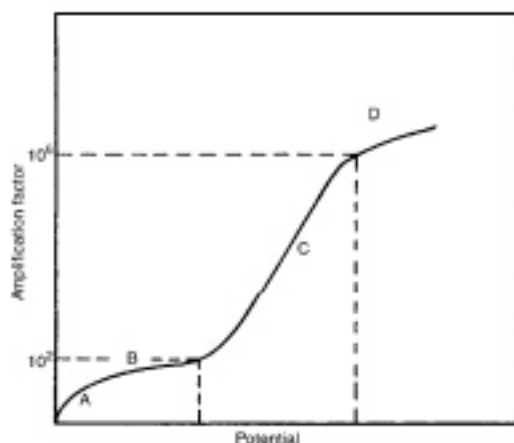
Figure 8.22   Gas-filled detector response vs. potential. A detector operating at the plateau marked B is an ionization counter. A proportional counter operates in the sloping region marked **C** where the response is proportional to the energy of the incoming photon. The plateau marked D represents the response of a Geiger counter. (Modified from Helsen and Kuczumow, used with permission.)

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 Fig. 8.22, 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 100 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 much 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.

8.2.4.4.   *Escape Peaks*

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:

$$E' = E \text{ (incoming X-ray)} - E \text{ (filler gas characteristic X-ray)} \qquad (8.16)$$

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 $K\alpha$ escape peak or the argon escape peak). An escape peak appears at 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. Escape peaks form in proportional and scintillation counters and in semiconductor detectors.

8.2.4.5. Pulse Height Distribution and Selection

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 in a proportional 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 Fig. 8.23. 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 full-width at half-maximum (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 wavelength dispersive 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 selector**. A pulse height selector is an electronic circuit that throws away signals that are below and above a preselected
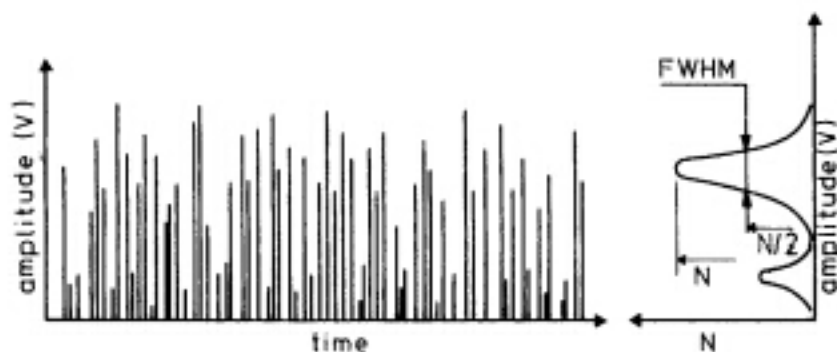
Figure 8.23 Amplitude or pulse height and time record of signals from the detector is on the left. Transformation of the data into a pulse height distribution is shown on the right. The FWHM measurement is shown for the higher peak. (From Helsen and Kuczumow, used with permission.)

energy window. It is very similar in its end result to the use of filters in UV/VIS spectrometers. The use of a pulse height selector in WDXRF eliminates noise as well as higher-order lines from the sample.
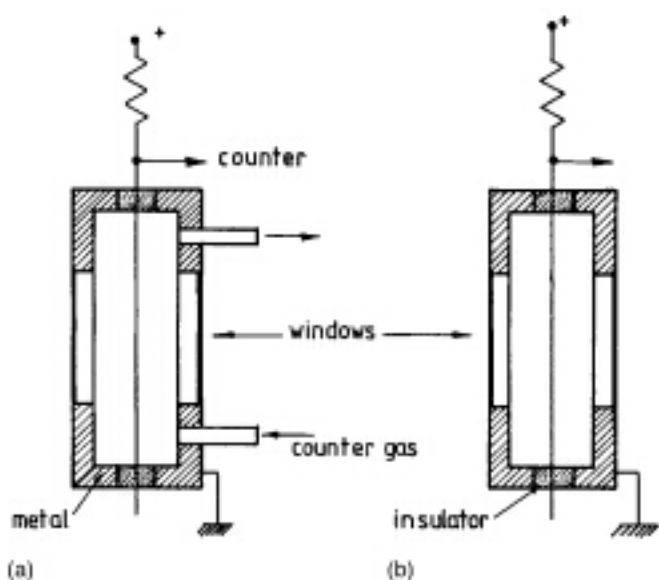
8.2.4.6. Proportional Counters

Flow Proportional Counter. The flow proportional counter covers a wide wavelength range and is generally used for wavelengths longer than 2 Å (elements with $Z < 27$). This detector is illustrated in Fig. 8.24(a). The windows are thin (<6 μm) polymer film, coated on the inside surface with aluminum to permit a homogeneous electric field to be established within the detector. 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 Fig. 8.24(a). The filler gas for a flow proportional counter is often 10% CH_4, 90% Ar, a mixture called P10 gas. The pressure, flow, and temperature of the gas must be precisely controlled for accurate detector response.

The operating voltage range for a flow proportional counter is 1–3 kV. As seen in Fig. 8.22, the amplification factor, which is the number of ion pairs discharged at the electrodes divided by the number of primary ion pairs formed, is 10^2–10^6. The current pulse is converted to a voltage pulse, is processed through a pulse height selector or discriminator and counted. Maximum count rate for a flow proportional counter is on the order of 2×10^6 cps.

Sealed Proportional Counter. A sealed proportional counter is shown schematically in Fig. 8.24(b). The windows are thicker, so they do not leak. Window materials include polymers, mica, aluminum, and beryllium. The filler gas used in a sealed proportional counter may be Ne, Kr, or Xe. Window and gas combinations are optimized for the wavelength of radiation to be detected; Al and Ne would be best for light elements, for example.

Multiple proportional counters are used in simultaneous X-ray spectrometers, while one proportional counter is often used in tandem with a scintillation counter in a sequential

Figure 8.24 Schematics of (a) a flow proportional counter and (b) a sealed proportional counter. (From Helsen and Kuczumow, used with permission.)