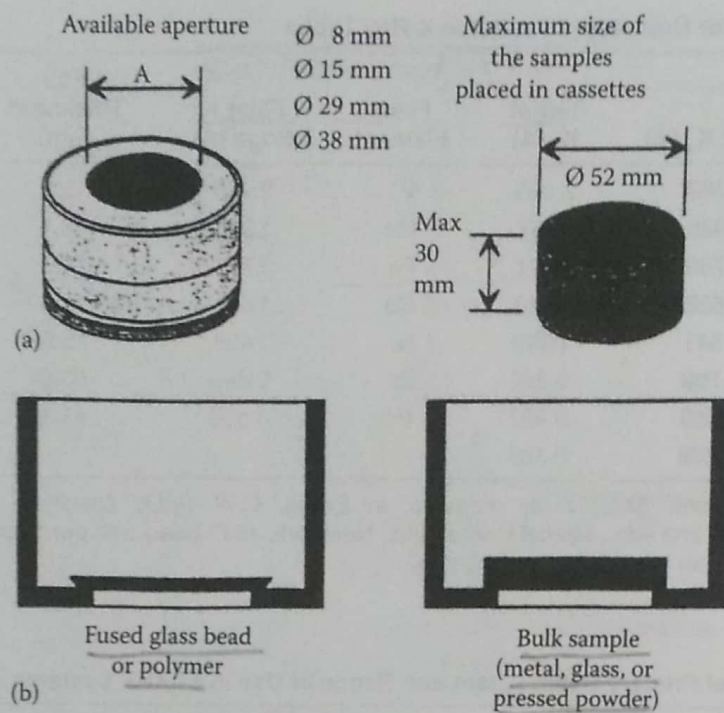


### 8.2.2.3 Sample Holders

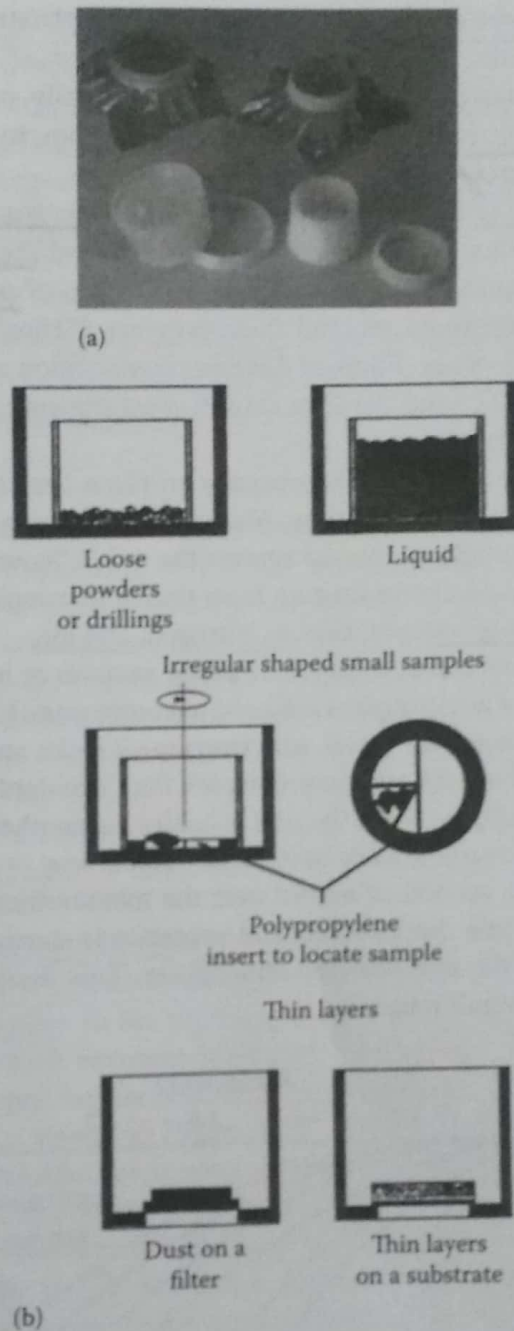
XRF is used for the analysis of solid and liquid samples, and similar sample holders and autosamplers are used for both EDXRF and WDXRF. Sample preparation and other considerations will be discussed in the applications section. For quantitative analysis, the surface of the sample must be as flat as possible, as will be discussed in the applications section. There are two classes of sample holders: cassettes for bulk solid samples and cells for loose powders, small drillings, and liquids. A typical cassette for a flat bulk solid such as a polished metal disk, a pressed powder disk, and a glass or polymer flat is shown in Figure 8.20a. The cassette is a metal cylinder, with a



**Figure 8.20** (a) Sample cassette for bulk solid samples. (b) Position of a bulk solid in the facedown configuration used in many spectrometers. (© Thermo Fisher Scientific. [www.thermofisher.com](http://www.thermofisher.com). Used with permission.)

*solid samples:*  
 screw top and a circular opening or aperture, where the sample will be exposed to the X-ray beam. The maximum size for a bulk sample is shown. The sample is placed in the cassette. For a system where the sample is analyzed facedown, the cassette is placed with the opening down and the bulk sample sits in the holder held in position by gravity, as shown in Figure 8.20b. If the system requires the sample faceup, the body of the cassette must be filled with an inert support (often a block of wood) to press the sample surface against the opening. These cassettes are available with a variety of apertures, usually from 8 to 38 mm in diameter, to accommodate samples of different diameters. Other types of solid samples, such as coatings on a solid substrate, can be placed directly in this type of cassette. *Liquid samples:*

The analysis of liquids, loose powders, or small pieces requires a different holder. The cells for these types of samples are multipart plastic holders, shown in Figure 8.21a, and require squares or circles of thin polymer film to hold the sample in the cell. The body of the cell is a cylinder open on both ends. One end of the cylinder is covered with the plastic film (or even clear plastic adhesive tape), and the film or tape is clamped into place by a plastic ring. The cell is placed with the film down, and the sample of liquid, powder, or filings is added. The film surface should be completely covered, as uniformly as possible. A plastic disk that just fits into the cell is inserted and pressed against the sample to obtain as flat a surface as possible, and a top cap is screwed or pressed on. For liquid samples, a vented top is used to avoid pressure buildup from heating of the sample by the X-ray beam. This assembled cell may be used "as is" or may be inserted into a standard cassette, as shown in Figure 8.21b in a facedown configuration. As you can imagine, if the thin polymer film breaks, samples of loose powder, chips, or liquid will spill into the interior of the spectrometer, contaminating the system and possibly breaking the Be window of the X-ray tube, if the tube is below the sample. It is for this reason that liquid sample cells are vented and a vacuum not used. This is the main disadvantage of the facedown configuration; for anything other than bulk samples, there is a risk of contaminating the instrument if the film covering the sample ruptures. Figure 8.21b shows that in the facedown configuration, a liquid



**Figure 8.21** Cells for liquid samples, loose powders, and chips. (a) Two types of disposable polyethylene sample cups for liquids and loose samples, consisting of a cup and snap ring to hold the polymer film cover. The cells with polymer film in place are shown at the top of the photograph. The disassembled cup and ring pieces are shown at the bottom of the photograph. (Courtesy of SPEX Certiprep, Inc. Metuchen, NJ. [www.spexcsp.com](http://www.spexcsp.com).) (b) Liquid and other loose samples in cells such as those shown in the photo, and then inserted into a sample cassette of the type shown in (a) for a facedown configuration spectrometer. As shown, dust sampled on impact filters or thin-layer samples may be inserted directly into the sample cassette. (© Thermo Fisher Scientific, [www.thermofisher.com](http://www.thermofisher.com). Used with permission.)

naturally assumes a flat surface. Imagine what the liquid sample would look like faceup. An air bubble will form at the film surface if a sealed cell is used and not filled completely. A bubble may form at the surface by heating of the sample in the X-ray beam if the cell is filled completely. If this occurs, the intensity of XRF from the sample will drop dramatically, and the possibility of film rupture as the pressure in the cell builds increases dramatically. So, if liquid samples

must be analyzed, the facedown configuration gives better quantitative results, even at the risk of contaminating the spectrometer. *position adjustment:*

The sample cassette is moved into position, either manually or with an automatic sample changer. In position, the sample is spun, generally at about 30 rpm, to homogenize the surface presented to the X-ray beam. *polyfilms:*

Polymer films used to cover the cell opening must be low in trace element impurities, strong enough to hold the sample without breaking, thermally stable, and chemically inert. They certainly must not be soluble in any liquid samples to be analyzed. Films of polyester (Mylar®), polyimide (Kapton®), polycarbonate, polypropylene, and fluoropolymer (Teflon®) are commonly used, with film thickness ranging about 3–8 μm. Films of different composition and thickness transmit X-rays to varying degrees (Figure 8.22), and the film chosen must transmit the wavelengths for the elements to be measured in the sample.

Manual XRF units are designed for the operator to place the sample into the measurement position, and this is done one sample at a time. Manual systems also include handheld XRF (HH XRF) analyzers, where the sample is pressed against the unit's "nose," with no sample holder (or preparation). The sample position and beam path from source to sample and detector accommodate different atmospheres, including vacuum, helium, nitrogen, and air.

### 8.2.2.4 EDXRF Detectors

The detector is the most crucial component of the EDXRF unit since it detects and sorts the incoming photons originating from the sample. The detector type and associated electronics determine the performance with respect to count rate, resolution, and detection efficiency. *Count rate:*

The count rate is the total of all photons detected and counted by the detector over the energy range being detected. *Kinds of detector:*

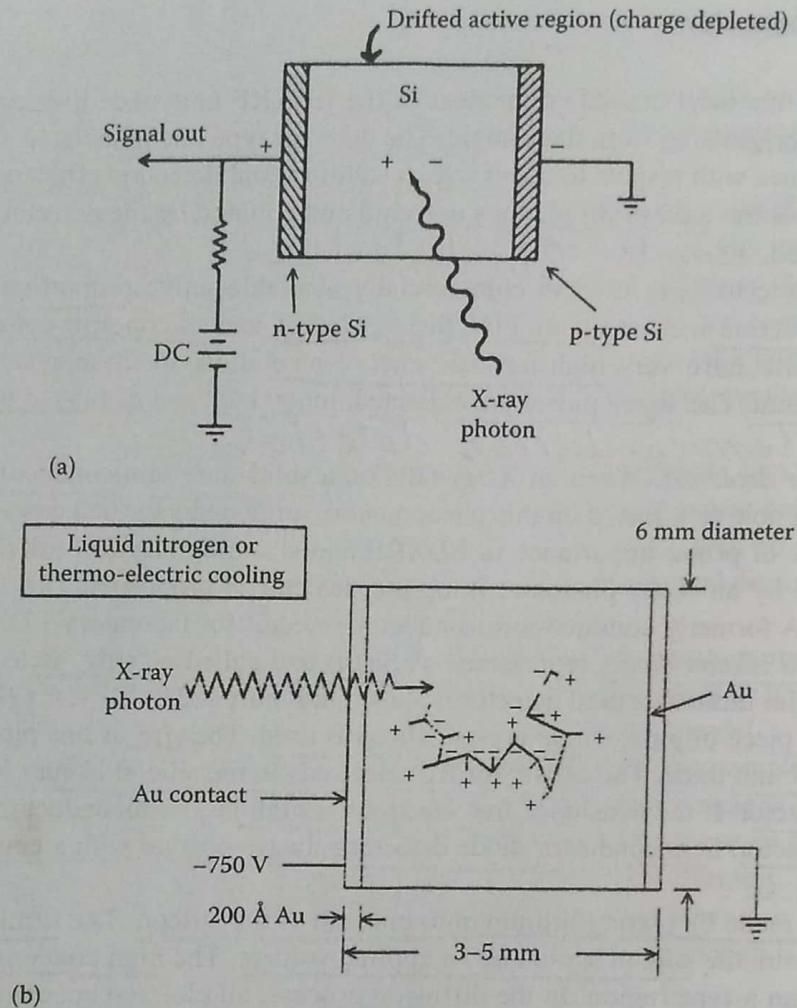
Two type of detectors are used in commercially available units: proportional detectors and semiconductor detectors such as silicon PIN, Si(Li), Ge(Li), and silicon drift detectors. The detectors used in EDXRF have very high intrinsic energy resolution. In these systems, the detector resolves the spectrum. The signal pulses are collected, integrated, and displayed by a multichannel analyzer (MCA). *Semiconductor detectors:*

*Semiconductor detectors.* When an X-ray falls on a solid-state semiconductor, it generates an electron ( $e^-$ ) and a hole ( $e^+$ ). Based on this phenomenon, semiconductor detectors have been developed and are now of prime importance in EDXRF and scanning electron microscopy. The total ionization caused by an X-ray photon striking the detector is proportional to the energy of the incident photon. A formerly common semiconductor detector for laboratory EDXRF systems was the lithium-drifted silicon diode, represented as Si(Li) and called a "silly" detector. A schematic diagram of a silicon lithium-drifted detector is shown in Figure 8.23. *Si cylinder:*

A cylindrical piece of pure, single-crystal silicon is used. The size of this piece is 4–19 mm in diameter and 3–5 mm thick. The density of free electrons in the silicon is very low, constituting a p-type semiconductor. If the density of free electrons is high in a semiconductor, then we have an n-type semiconductor. Semiconductor diode detectors always operate with a combination of these two types. *Diode:*

The diode is made by plating lithium onto one end of the silicon. The lithium is drifted into, that is diffused into, the silicon crystal by an applied voltage. The high concentration of Li at the one end creates an n-type region. In the diffusion process, all electron acceptors are neutralized in the bulk of the crystal, which becomes highly nonconducting. This is the intrinsic material. The lithium drifting is stopped before reaching the other end of the silicon crystal, leaving a region of pure Si (p-type), as shown in Figure 8.23. Submicron gold layers are applied at each end as electrical contacts. The detector is reverse-biased, removing any free charge carriers from the intrinsic region. Under this condition, no current should flow since there are no charge carriers in the intrinsic region. However, the bandgap between the valence band and the conduction band is small, only 1.1 eV for Si(Li). At room temperature, thermally generated charge carriers cross this barrier easily and become conductive even with no X-ray photons striking the detector. This causes a high noise level. To decrease this noise and increase the sensitivity of the detector, the temperature of the system must be decreased significantly. This is accomplished by cooling the detector to 77 K with liquid nitrogen, which must be replenished regularly. Peltier effect-based electronic cooling is used with temperatures of as low as  $-90^\circ\text{C}$  on benchtop EDXRF units. A Peltier cooling device, also known as a thermoelectric cooling device, uses the Peltier effect to create a heat flux between the junction of two different materials. A Peltier cooler is a solid-state heat pump, which transfers heat from one side of the device to the other, depending on the direction of the electric current. The solid-state nature of the cooler means no moving parts, compact size, and no maintenance. These devices are commonly used to cool electronic components. *Germanium (Li) drift detector:*

In exactly the same fashion, germanium, also in group IV of the periodic table, can be used instead of silicon, making a Ge(Li)-drifted detector. (You might guess this is called a "jelly" detector.) The Ge(Li) detector also requires liquid nitrogen or electronic cooling, since its bandgap is only 0.66 eV.



**Figure 8.23** The Si(Li) semiconductor detector. (a) Schematic shows the n-type Si region on one end of the Si crystal, a central charge-depleted intrinsic region and p-type Si on the other end. (b) The actual detector has 200 Å layers of gold as electric contacts on each end of the crystal. An X-ray photon striking the intrinsic region generates electron-hole pairs within the diode. (b: © Thermo Fisher Scientific. [www.thermofisher.com](http://www.thermofisher.com). Used with permission.)

*working:*

An X-ray photon striking the detector produces multiple electron-hole pairs in the intrinsic region (Figure 8.23b). The number of electron-hole pairs produced is proportional to the photon energy. The energy required to make an electron-hole pair is 3.86 eV in Si(Li), so the number of electron-hole pairs formed is approximately

$$n = \frac{E}{\epsilon} = \frac{E}{3.65 \text{ eV}} \quad (8.16)$$

where

$n$  is the number of electron-hole pairs

$E$  is the energy of the incident X-ray photon (eV)

$\epsilon$  is the energy to form an electron-hole pair (eV)

For a similar Ge lithium-drifted detector, the energy required for ionization is 2.96 eV. This is much less than the energy required for ionization in a proportional counter or a NaI(Tl) scintillation detector.

Under the influence of an applied voltage, the electrons move toward the positive end and the holes toward the negative end of the detector. The total charge collected at the positive contact is

$$Q = nq_e \tag{8.17}$$

where

$Q$  is the total charge in coulombs (C)

$n$  is the number of electron-hole pairs =  $E/e$

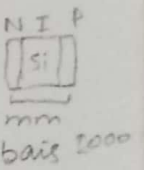
$q_e$  is the charge on one electron =  $1.69 \times 10^{-19}$  C/electron

$Q \propto E \text{ photon} \propto V$

The collection of charge results in a voltage pulse. Since the total charge is proportional to the energy of the incident photon, the amplitude of the voltage pulse produced is also directly proportional to the energy of the incident photon. The voltage pulses are amplified and "shaped" electronically and sent to a multichannel pulse height analyzer (Section 8.2.2.5) to be sorted by pulse height and counted.

*Si PIN diode detector:*

**Silicon PIN diode detectors.** These consist essentially of a couple of mm thick silicon junction type p-i-n diode with a bias of 1000 V across it. The heavily doped central part forms the nonconducting i-layer (intrinsic layer), where the doping compensates the residual acceptors that would otherwise make the layer p-type. When an X-ray photon passes through, it causes a swarm of electron-hole pairs to form, and this causes a voltage pulse. To obtain sufficiently low conductivity, the detector must be maintained at low temperature with a Peltier device. Continuous improvement of the pulse processing results in resolution as low as 125 eV. Count rate and resolution are strongly correlated; the resolution is best at a low count rate. The yield of this detector for higher energies is good although less than the Si(Li) detector (Figure 8.24).



$\text{Resolution} \propto \frac{1}{\text{count rate}}$

**Silicon drift detector.** Commercially available silicon drift detectors (SDDs) are based on the drift chamber principle. The detector crystal is moderately cooled by vibration-free thermoelectric coolers. A monolithically integrated on-chip field effect transistor (FET) acts as a signal amplifier and controls energy resolution. The sideward depletion of the active detector volume in connection with the integrated drift structure provides an extremely small detector capacitance that enables the use of fast signal processing techniques, thus enabling high count rate processing. The processing electronics enable high count rate and the lowest possible resolution (Figure 8.25).

The unique property of this type of detector is the extremely small value of the anode capacitance, allowing the FET to be either integrated on the chip or connected to it by a short metal strip.

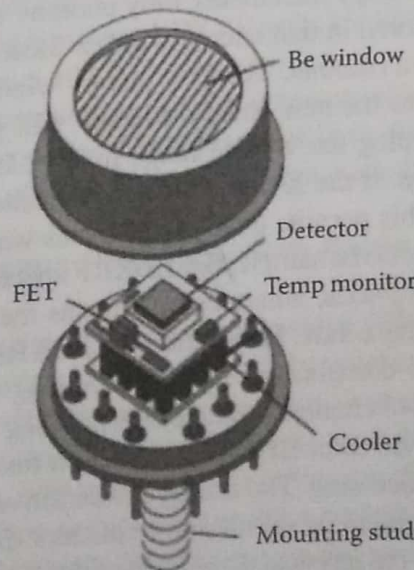
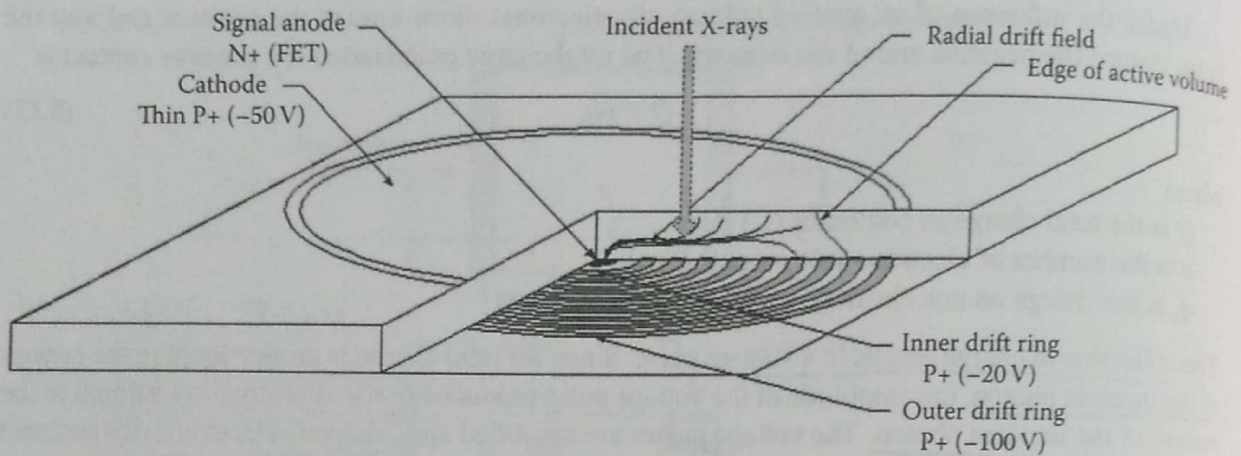


Figure 8.24 Schematic of a silicon PIN detector. (Courtesy of Amptek, Inc. www.amptek.com.)



**Figure 8.25** Schematic of an SDD. (Courtesy of Amptek, Inc. [www.amptek.com](http://www.amptek.com).)

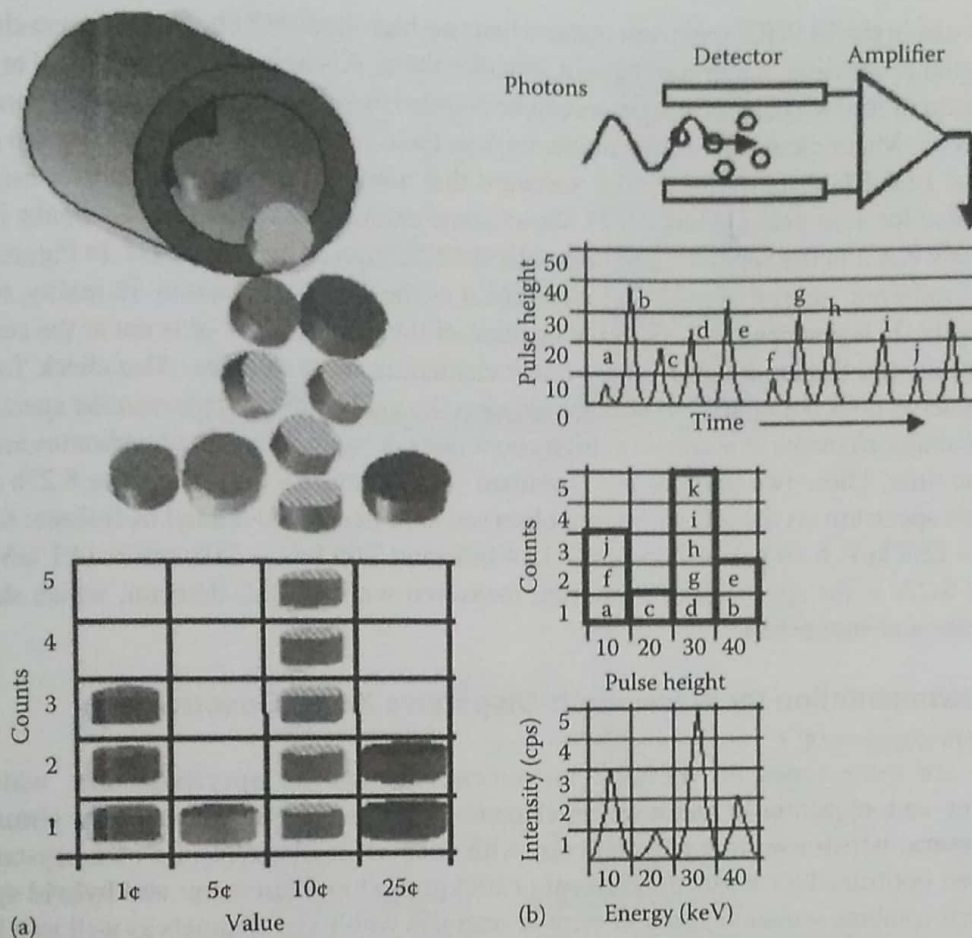
Using very elaborate and proprietary processing technology in the fabrication reduces the leakage current level to such low levels that the detector can be operated with moderate cooling. This cooling can be readily achieved by Peltier cooling and is in the vicinity of  $-15$  to  $-20^{\circ}\text{C}$ .

### 8.2.2.5 Multichannel Pulse Height Analyzer

A multichannel pulse height analyzer, also called a multichannel analyzer (MCA) or digital pulse processor, collects, integrates, and displays the signal pulses from the detector. The operation of an MCA can be modeled in a simple fashion. Assume we have a handful of coins of different denominations and a coin-sorting device to put each coin into a separate stack (Figure 8.26a). The stacks will have different heights, depending on the number of coins of each type (Figure 8.26b, second plot from the bottom). We can plot "counts" or number of coins versus the height of the stack. An MCA does the same thing with photons of different energies. Assume that we have a pulse height analyzer of a given total voltage range with the ability to change the voltage in small increments. As an example, the total voltage range is 10 V, and the interval of change is 0.1 V. X-rays of short wavelengths (high energies) must be separated from X-rays of long wavelengths (low energies). That is what a pulse height analyzer does; it rejects energy signals that are higher or lower than a selected energy window. If the analyzer window can be changed in small energy increments, only photons with that energy will pass through. Those photons are counted and stored in that energy window location in the analyzer memory. Each energy window location is called a *channel*. Then the energy window (voltage) is changed by 0.1 V, and only photons corresponding to the new energy window will pass through and be counted and stored in a second channel. Sweeping the voltage range in steps of 0.1 V permits us to distinguish between X-rays of various energies. If the X-ray photons are counted by energy, we can obtain  $I$ , the X-ray intensity at given energy. This permits us to plot  $I$  versus wavelength (energy), which gives us an energy spectrum of the XRF from the sample. An EDXRF spectrum is in the form of a histogram, usually plotted as "counts" on the y-axis, where counts means the number of photons counted in a given channel, versus energy on the x-axis. In practice, an EDXRF is equipped with a pulse height analyzer with many channels and complicated signal processing circuitry. A typical multichannel pulse height analyzer may have 2048 channels, each corresponding to a different energy interval.

Resolution in a semiconductor detector EDXRF system is a function of both the detector characteristics and the electronic pulse processing. The energy resolution of semiconductor detectors is much better than either proportional counters or scintillation counters (SCs). Their excellent resolution is what makes it possible to eliminate the physical dispersion of the X-ray beam; without the energy resolution of semiconductor detectors, EDXRF would not be possible. Resolution is generally defined as the smallest energy difference observable between peaks. In EDXRF, the energy resolution is defined





**Figure 8.26** Schematic of the pulse processing of an MCA. (a) The "coins" (photons) are separated by denomination and binned. (b) second from the bottom: The number of coins gives a "stack height" (counts). The typical EDXRF output is the lower-right plot of counts per second versus energy.

as the FWHM of the Mn K emission peak. Resolution is dependent on the energy of the detected photon and due to the pulse processing also depends on the total number of photons counted (total input count rate). The area of the detector as well as the electronic parameters of the pulse processor affect resolution as well and need to be included in a complete system comparison.

The most common detectors in benchtop EDXRF units are SDDs of  $<10 \text{ mm}^2$  area with a resolution of  $<150 \text{ eV}$  for the Mn K line at 100,000 counts/s.

In handheld or portable instrumentation, Si-PIN detectors of  $<10 \text{ mm}^2$  area are common, with a resolution of  $<170 \text{ eV}$  at 40,000 cps. For the detection of light elements (Mg to S), SDDs are more suitable and achieve a resolution of  $<190 \text{ eV}$  at 90,000 cps with detector areas of  $\geq 25 \text{ mm}^2$ .

### 8.2.2.6 Detector Artifact Escape Peaks and Sum Peaks

{ Spectrum artifacts may appear in the energy-dispersive (ED) spectrum. These are peaks that are not from elements in the sample, but are caused by interaction between the sample and the detector material. For example, when measuring pure iron or steel, some of the Fe photon energy is transferred to the Si detector atoms; the amount of energy absorbed by a Si atom has *escaped* from the Fe photon. This type of peak, which may appear in the spectrum, is called an escape peak. The Si escape peak, from the Si  $K_\alpha$  line, results in an artifact peak 1.74 keV lower than the parent peak when any silicon-based detector is used. Similar escape peaks at different energies appear for Ge if a Ge detector is used. Table 8.A.2 in the appendix gives the keV values for the K and L lines of all the elements and can be used to calculate where an escape peak might appear in the spectrum.

Sum peaks in the EDXRF spectrum occur when two high-intensity photons arrive so close in time that the signal processing electronics cannot separate them. A single peak is registered at an energy that is the sum of the two peaks. Sum peaks can be avoided by reducing the current and thus the signal on the detector. Major elements in the sample, such as Fe in steel, are generally the source of the sum peaks. Most EDXRF systems come with software that automatically can correct for escape peaks and some also for sum peaks.) Figure 8.27 shows some examples of these artifact peaks in EDXRF spectra. Table 8.A.2 in the appendix can help with identification of these artifacts. In Figure 8.27a, the instrument software “marks” a peak and identifies it as the element francium. In reality, the peak at 2.77 keV is the Ti  $K_{\alpha}$  escape peak. Note the position of the marker line—it is not at the center of the emission peak, and francium is not a very likely element in most samples. Also check Table 8.A.2. The peak energy does not match Fr. This should alert the analyst to an artifact in the spectrum.

For the major elements in a sample at high count rates, it is possible that two photons are detected at the same time. These two photons are “summed” in the detector output. Figure 8.27b shows the Fe emission spectrum on the left with three observed sum peaks, calculated as follows:  $6.40 \text{ keV} + 6.40 \text{ keV} = 12.8 \text{ keV}$ ;  $6.40 \text{ keV} + 7.05 \text{ keV} = 13.4 \text{ keV}$ ; and  $7.05 \text{ keV} + 7.05 \text{ keV} = 14.1 \text{ keV}$ .

Figure 8.27c is the spectrum of pure iron, measured with a Si(Li) detector, which shows both escape peaks and sum peaks.