

system. It is for this reason that the detector has two windows as shown in Fig. 8.24. X-ray photons pass through the proportional counter to the scintillation counter located behind it, as illustrated in Fig. 8.15 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.

Scintillation Counter. 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.

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 Tl in the crystal lattice is coupled to a PMT, shown in Fig. 8.25. When an X-ray photon enters the crystal, it causes the interaction



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

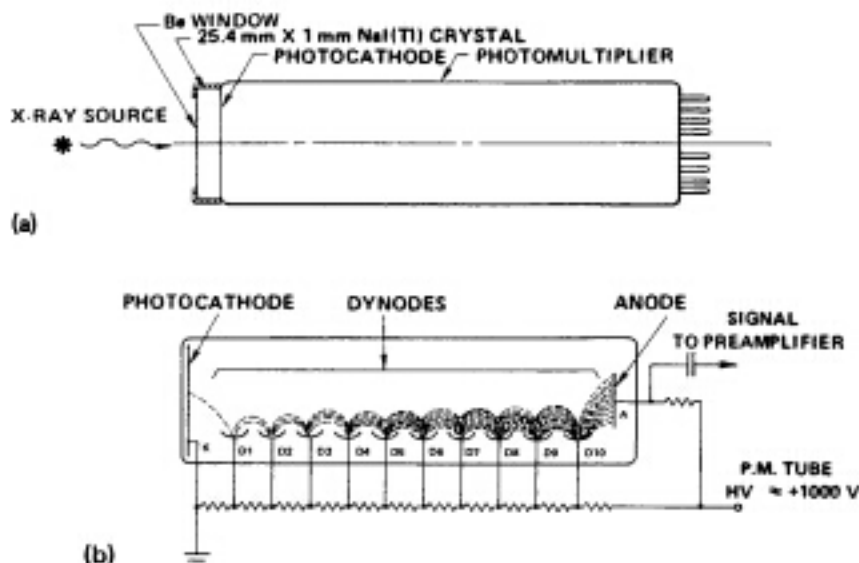


Figure 8.25 The NaI(Tl) scintillation detector. (a) The assembled detector; (b) a schematic representation of the photomultiplier and its circuitry. [Courtesy of ORTEC (Ametek) (www.ortec-online.com). From Jenkins et al., 1981, used with permission.]

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, $< 2 \text{ \AA}$ ($Z > 27$), 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 \AA). Incoming X-rays with wavelengths less than 0.374 \AA 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 results in the output pulse because of the multiple steps involved in the operation of this detector.

8.2.5. Sample Holders

XRF is used for the analysis of solid and liquid samples. 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, a glass or polymer flat is shown in Fig. 8.26(a). The cassette is a metal cylinder, with a 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 face down, the cassette is placed with the opening down and the

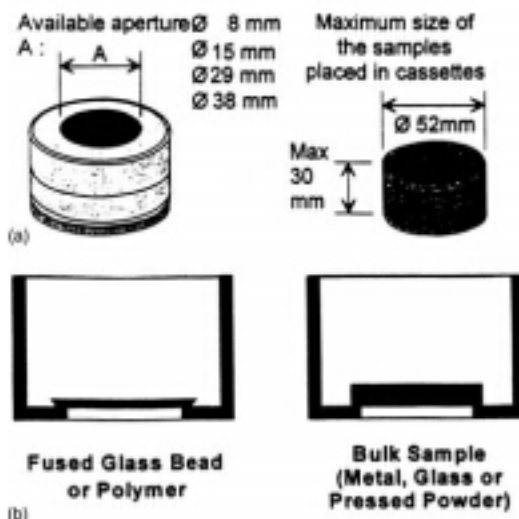


Figure 8.26 (a) Sample cassette for bulk solid samples. (b) Position of a bulk solid in the face-down configuration used in many spectrometers. [Courtesy of Thermo ARL (www.thermoARL.com).]

bulk sample sits in the holder held in position by gravity, as shown in Fig. 8.26(b). If the system requires the sample face up, 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.

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 Fig. 8.27(a) 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

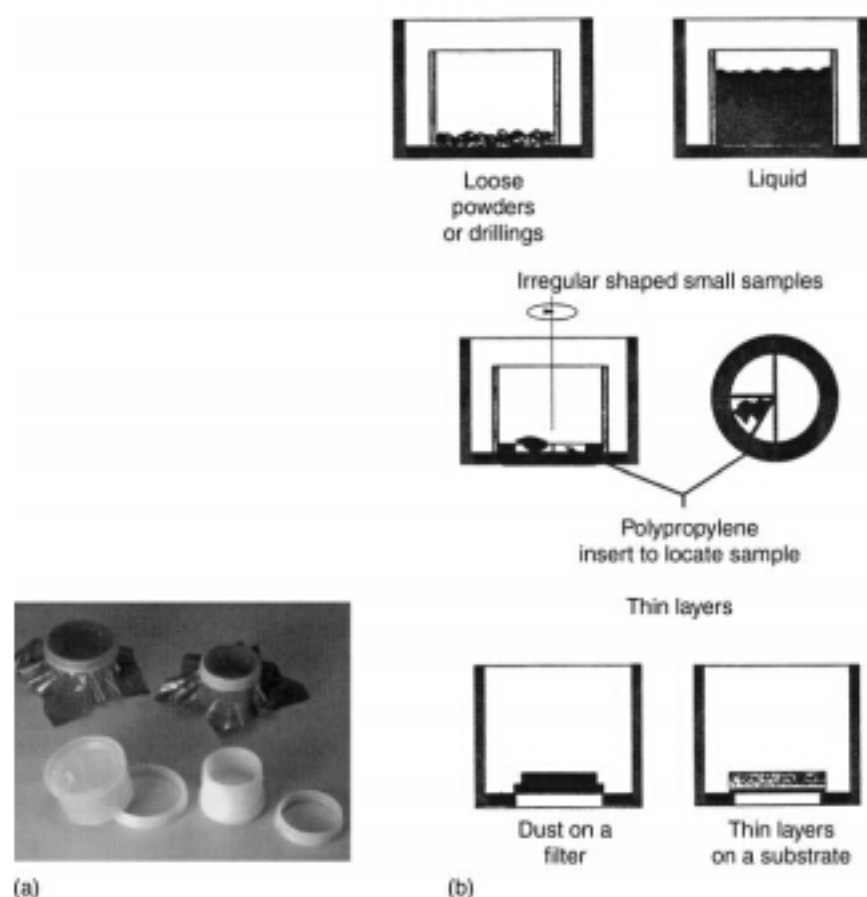


Figure 8.27 Cells for liquid samples, loose powders and chips. (a) Two types of disposable polyethylene sample cups for liquids and loose samples, consisting of a cup and snap-ring to hold the polymer film cover. The cells with polymer film in place are shown at the top of the photograph. The disassembled cup and ring pieces are shown at the bottom of the photograph. [Courtesy of SPEX Certiprep, Inc. Metuchen, NJ (www.spexcsp.com).] (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 Fig. 8.26(a) for a face-down configuration spectrometer. As shown, dust sampled on impact filters or thin layer samples may be inserted directly into the sample cassette. [Courtesy of Thermo ARL (www.thermoARL.com).]

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 build-up 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 Fig. 8.27(b) in a face-down 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 analyzing crystal and the rest of 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 samples cells are vented and that a vacuum is not used. This is the main disadvantage of the face-down configuration; for anything other than bulk samples, there is a risk of contaminating the instrument if the film covering the sample ruptures. Figure 8.27(b) shows that in the face-down configuration, a liquid naturally assumes a flat surface. Imagine what the liquid sample would look like face-up. 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 X-ray fluorescence 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 face-down configuration gives better quantitative results, even at the risk of contaminating the spectrometer.

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

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 (Fig. 8.28), and the film chosen must transmit the wavelengths for the elements to be measured in the sample.

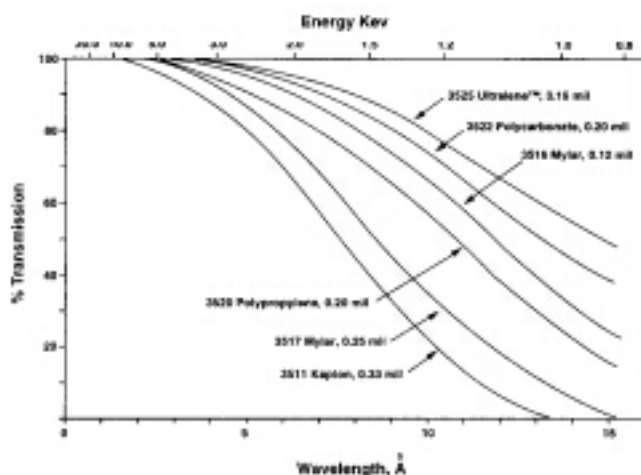


Figure 8.28 The X-ray transmission characteristics of some thin polymer films used as sample holder covers for liquid, loose powder, and similar samples. [Courtesy of SPEX Certiprep, Inc. Metuchen, NJ (www.spexcsp.com).]

8.2.6. Simultaneous WDXRF Spectrometers

A simultaneous WDXRF system uses multiple channels, with each channel having its own crystal/detector combination optimized for a specific element or background measurement. Instruments with as many as 40 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 for the same suite of elements every day. They have the advantage of being very fast compared with a sequential system, but are not flexible.

Most simultaneous systems have the X-ray tube above the sample, with the sample facing up. As discussed earlier, this makes the analysis of liquids difficult or impossible. Several instrument manufacturers offer combination systems with a simultaneous set of channels as well as a sequential monochromator. These systems offer the speed needed for routine analysis and the flexibility needed for nonroutine analysis, but are expensive.

8.2.7. EDXRF Spectrometers

In EDXRF spectrometry, there is no physical separation of the fluorescence radiation from the sample. There is no dispersing device prior to the detector, as seen in Fig. 8.29. All of the photons of all energies arrive at the detector simultaneously. The semiconductor detector used in EDXRF is a proportional detector with very high intrinsic energy resolution. In this system, the detector resolves the spectrum. The signal pulses are collected, integrated and displayed by a multichannel analyzer (MCA). As Fig. 8.29 shows, a primary beam filter is often used to improve the signal-to-noise ratio for given energy regions. As with WDXRF systems, most EDXRF systems have a series of selectable filters. Typical filters used in EDXRF and their ranges of use are listed in Table 8.7.

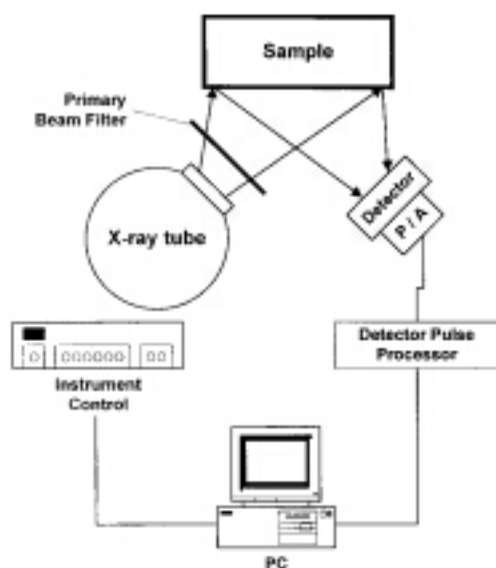


Figure 8.29 A schematic energy dispersive XRF system with an X-ray tube source. There is no dispersion device between the sample and the detector. Photons of all energies are collected simultaneously. (From Ellis, used with permission.)