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clean pinhole with a sewing needle in a lead sheet. The size of the hole should be representative of an X-ray spot, say 0.3 mm in diameter. The mask should be firmly and reproducibly secured a few cm from the fluorescent source at a wide angle to the incident beam. Using a scintillator/phototube combination, measure the number of X-rays per second emerging through the hole at a given X-ray source loading. A sufficient number of X-rays per measurement (say 10^5) is necessary to obtain accurate statistics (0.3%). This measurement should be repeated to verify the stability of the source.

This spot can now be recorded by the detector in question, using different integration times to vary the dose. 20 measurements at each integration time should give a reliable measure of the standard deviation in the signal. It is vital to move the position of the spot on the detector face for each exposure, taking care to move only the detector without disturbing the remainder of the experimental setup. Only by moving the detector is the fidelity of the calibrations tested. One subtlety is that the sensitivity of many detectors varies with the angle of incidence of the X-rays, so that it will be necessary to vary both the position and angle of the detector between exposures.

By using a wide range of integration times, both the sensitivity of the detector at low doses and the ultimately achievable measurement accuracy can be examined. These data may also highlight specific problems a detector might have, such as nonlinearity.

The DQE can be measured for a spot in the presence of a background if the lead pinhole mask is now replaced with a pinhole in a semitransparent aluminium foil. Choose the foil thickness to yield an appropriate background level, say 20% of the pinhole intensity. The uncertainty in the measurement of the spot intensity now results from the total counts in the integration area in addition to the uncertainty in determining the background. A wide PSF is especially harmful in this case, since many more pixels must be integrated to encompass the spot.

These evaluation procedures test only limited aspects of the detector, but in doing so, much is learned not only about the detector, but also about the degree to which the vendor is willing to work with the user, which is clearly of interest. The ultimate test for a crystallographer is whether a detector delivers good data in a well understood experimental protocol. Usually, values of $R_{\rm sym}$, the agreement of integrated intensities from symmetry-related reflections, are evaluated as a function of resolution. Low values of $R_{\rm sym}$ suggest good quality data. A much more stringent test can be made by comparing anomalous difference Patterson maps based on the Fe atom in myoglobin (Krause & Phillips, 1992). The limitation in these crystallography-based evaluations is that they tend to rely on robust, strongly diffracting crystals, which allow accumulation of good X-ray statistics even with insensitive detectors. Weakly diffracting and radiation-sensitive crystals are less forgiving.

7.1.3. Characteristics of different detector approaches

7.1.3.1. Point versus linear versus area detection

A point detector may be based on a scintillating crystal or a gas-filled counter, with the sensitive area defined by slits or a pinhole mask. The spatial resolution of such a detector can be made arbitrarily fine at the expense of data collection rate. Point detectors can have very high accuracy if the background is removed by energy discrimination. They find application in powder diffractometry and small-molecule crystallography, in which the reflections are widely dispersed, thereby simplifying measurement of individual reflections. Clearly, specimen and source stability are important for such work.

Throughput can be greatly increased by area detection, which is often required for macromolecular crystallography or investigations of unstable specimens. Typical area detectors, such as film, storage phosphors and charge-coupled devices (CCDs), are described below.

7.1.3.2. Counting and integrating detectors

Detectors can be broadly divided into photon counters and photon integrators. Photon counters have the advantage that some designs permit energy discrimination, allowing them to reject inelastically scattered radiation, thereby improving the signal-to-noise ratio. However, photon-counting detectors always have a count-rate limitation, above which they begin to miss events, or even become unresponsive (the time during which a detector misses events is known as dead time). Prototype systems have demonstrated linear count rates greater than 10^6 photon s^{-1}. Fabrication difficulties have limited the commercial availability of photon-counting detectors with large areas, high spatial resolution and high count rates. The count rate is a particular concern at modern synchrotron sources, which are capable of generating diffraction that delivers two or more photons to a pixel during one bunch time, an instantaneous count rate greater that 10^{10} photons per second per pixel. Integrating detectors are more typically used in situations where very high event rates are expected.

In contrast, integrating detectors have no inherent count-rate limitation, though at very high fluxes several sources of nonlinearity can theoretically become important, such as nonlinearity in the phosphor used to convert the X-ray image to a visible image. Integrating detectors, however, do not discriminate energy, and they have noise that increases with integration time. Nonetheless, film, image-plate and CCD integrating detectors are currently commercially available and in widespread use.

7.1.3.2.1. Photon-counting detectors

Commonly used photon counters include *scintillator/photomultiplier combinations*, *gas-filled counters* and *reverse-biased semi-conductor detectors*.

Scintillator/photomultipliers usually consist of a relatively thick crystal of a scintillator coupled to a high-gain photomultiplier tube. These detectors are generally designed to serve as point photon counters with moderate energy resolution. In order to perform this function, several constraints must be met:

(1) The scintillator crystal must be thick enough to have almost unity stopping power.

(2) It is necessary to collect as many of the converted visible photons as possible, so an optically clean scintillator crystal is used in a reflective housing to direct as many photons as possible toward the phototube.

(3) The scintillator must emit its light quickly, so as to minimize dead time, and be efficient, so as to emit much light. NaI:Tl, CsI:Na and CsI:Tl meet these constraints. NaI is more commonly used, but CsI may be preferred at higher X-ray energies because of its higher stopping power. Both materials are hygroscopic and are usually encased in hermetically sealed capsules with beryllium windows.

(4) The phototube is usually operated in its linear region for energy discrimination.

Scintillator/phototube combinations are relatively trouble-free and often have near-unity DQE. Their main limitations are count rates well below 10^6 photon s^{-1} and the lack of spatial resolution. Even so, such detectors are still preferred in many applications where the data are effectively zero- or one-dimensional.

Reverse-biased semiconductor detectors are designed to have a thick depletion zone in which charge can be efficiently collected and conveyed to an amplifier. X-rays that stop in the depletion zone produce electron–hole pairs; these are separated by the depletion zone field and the electrons are swept to the input of a low-noise amplifier. Single-photon counting can be readily achieved, even for low-energy X-rays, especially if the detector is cooled to minimize thermally generated charge. These detectors are typically fabricated as silicon diodes, but germanium and gallium arsenide are also used (Hall, 1995). Until recently, these devices were generally configured as point detectors or strip detectors consisting of a linear array of narrow sensitive regions, forming a one-dimensional detector (Ludewigt *et al.*, 1994). Two-dimensional arrays of square pixels are being developed, *e.g.* see the description of pixel array detectors below. In another device, the silicon drift detector, potentials are arranged in the silicon to funnel signals from a large area to a low-noise collection point (Rehak *et al.*, 1986). Such devices are being developed for both linear and area applications.

By increasing the electric field strength in an appropriately designed p-n junction in silicon, avalanche multiplication of the X-ray-induced electrons can be obtained as they move toward the anode where they are collected. This gives rise to a very high linear signal gain, with high speed and low noise. Arrays of such *avalanche photodiodes* as large as 8×8 elements, each 1×1 mm square, have been fabricated (Gramsch *et al.*, 1994; Farrell *et al.*, 1994).

Gas discharge (wire) counters make use of the ionization produced when an X-ray is stopped in the high-atomic-number gas, usually xenon, that fills the detector. A strong electric field between a fine anode wire and a cathode plane accelerates the products of the primary ionization to produce an ionizing multiplication (either a proportional or an avalanche discharge, depending on the field strength) that is detected as a charge pulse on one or both of the electrodes. The discharge is quenched by the presence of a few per cent of a second gas, *e.g.* methane or carbon dioxide. Gas discharge detectors have been configured in zero-, one- and two-dimensional versions and continue to be widely used in some applications. The venerable Geiger counter is in this class and is used for radiation monitoring and beam alignment in home laboratories. Properly designed gas discharge counters have very low noise, but the quantum efficiency depends critically on design, gas and X-ray energy.

Linear wire detectors have been used to record small-angle X-ray scattering. The localization of the X-ray event along the length of the detector is often performed by measuring the difference in arrival time of the charge pulses at the two ends of one of the electrodes (Barbosa *et al.*, 1989). The pulses are stretched to permit this measurement. One design uses a resistive anode wire to perform this function, whereas others configure the cathode plane as a delay line. Various two-dimensional arrangements of crossed planes of wires, broadly classified as multiwire proportional counters (MWPCs), have been widely used in crystallography, and some types have been commercially successful (Hamlin *et al.*, 1981; Blum *et al.*, 1987).

The design of MWPC area detectors has had difficulty keeping up with improvements in X-ray sources, particularly the high fluxes available at storage rings, and the shift toward use of higher-energy X-rays. The electric discharge at the heart of the technology has an inherent dead time associated with it. Added to this inherent dead time are the pulse propagation and processing times which limit the counting rate for a given wire. Thus, MWPCs are subject to a severe count-rate limitation. A second limitation of MWPCs has been their large pixel size and the relatively small number of pixels across the detector face, as well as parallax effects. These problems have been addressed by changes in the detector geometry (*e.g.* spherical drift chambers; Charpak, 1982), by microfabrication on glass substrates of the wires comprising the back plane of the detector, and by dividing the active area into small zones, each of which is read out independently. Robustness of MWPCs has also been a problem.

The dead time can be reduced by reducing the thickness of the detector. However, reducing the detector thickness reduces the X-ray stopping power. Increasing the gas pressure not only improves the quantum efficiency, but also helps to reduce the dead time further. Unfortunately, high gas pressure complicates the design of the front window of the detector. Despite these problems, two-dimensional gas-detector prototype modules with 200 μm square pixels have been constructed that are expected to have a local linear count-rate limit of 7 MHz mm^{-2} and a quantum efficiency above 80% at energies used in crystallography (see Sarvestani *et al.*, 1998).

7.1.3.2.2. Integrating detectors

X-ray film was the first area detector and has a long history of important contributions to the solution of structures and to X-ray imaging (Arndt *et al.*, 1977). In many applications, film has effectively been displaced because of its relative insensitivity caused by the high level of background fog, its multistep processing leading to long delays before digital data are obtained and its nonlinearity. However, X-ray film is still a superior integrator for long exposures, and lithographic film has much higher spatial resolution than any other area detector. Polaroid film in an X-ray cassette is an excellent diagnostic tool for beam alignment problems. And, in all cases, film is inexpensive.

Storage phosphors, also called image plates, are probably the most widely used area X-ray detector for crystallography at present, particularly in laboratories with conventional X-ray sources (Amemiya *et al.*, 1988; Eikenberry *et al.*, 1992). These sheets of material are a much improved functional replacement for X-ray film in many applications, including medical radiography and autoradiography in biological research. Storage phosphors are made from a BaFBr:Eu or other photostimulable phosphor coated on a suitable backing. These phosphors have the property that absorbed X-ray energy can be trapped in long-lived states within the phosphor grains, and that this energy can later be released as blue fluorescence upon photostimulation with red light. Grain-size distribution, grain orientation, binder choice and coating thickness are important parameters in the commercial preparation of the sheets.

The exposed phosphor sheet is raster-scanned with a finely focused red laser and the resulting photostimulated emission is recorded by a photomultiplier. The result is a digital image of the X-ray intensity distribution. The scanning can be done either on-line in self-contained systems or off-line in a separate scanning instrument. Scanning typically requires several minutes. In advanced scanners, this is reduced to several tens of seconds, where the limit is set by the time constant of the photostimulated emission process, which in turn determines the minimum time the laser should dwell on each pixel. The off-line scanner, preferred at synchrotron sources, permits a new exposure to be made while scanning is performed. Self-contained systems offer the advantages of simplified operation and the possibility of calibrating the detector, since only a single sheet of material is used in a mechanically stable setup.

Storage phosphors are typically read out with 100 µm square pixels, resulting in 2000 × 2500 pixel images for the common size of sheet. Larger formats are available. The wide PSF of storage phosphors makes the effective pixel size considerably larger than the nominal value. Some scanners permit smaller pixels, but this is of limited utility because there is a readout noise component associated with each pixel and too small a pixel harms the signal-to-noise ratio without improving data. The most critical component of the storage-phosphor system is the mirror assembly that gathers the photostimulated emission during readout. There are very few emitted photons for each stored X-ray (at the photon energies used for diffraction), and only a small fraction of these are detected in the photomultiplier (in some cases less than one per stored X-ray). This step in the detection process is critical in maintaining high quantum efficiency. Although image plates have an inherently wide dynamic range, the practical value is always limited by the scanner analogue-to-digital converter.

Television detectors. Numerous integrating detector designs based on television sensor technologies have been published and, in one case, produced commercially (Milch *et al.*, 1982; Arndt, 1991). These detectors span a wide range of design complexity and performance. The primary element is a phosphor screen, which converts the incident X-ray pattern to a light image that is directly or indirectly coupled to the sensor, such as a Vidicon or CCD. Many of the designs employ image intensifiers to raise the signal strength of the visible image above the noise of the sensor system. Some designs employ cameras operated at video rates, with frames accumulated in the attached computer or on videotape. Other designs use cooled cameras operated in a slow-scan mode, which greatly reduces noise. The X-ray exposure is integrated in the camera, then read out once at the end of the integration period.

Most of these systems would be classified as complex, but several of them are working reliably today in laboratories with conventional X-ray sources. The image intensifiers improve the DQE of the systems, while sacrificing dynamic range and image sharpness. In addition, intensifiers are sensitive to magnetic fields, requiring great care in their use if proper detector calibration is to be maintained.

Considerable enhancement to the television-type detector is made possible by the low-noise imaging capabilities of CCDs, described in Chapter 7.2. In this case, high DQE can be maintained without intensification when the CCD is cooled and read with slow-scan electronics. As such, these detectors are much more robust and have improved imaging qualities.

7.1.4. Future detectors

Commercially available X-ray detectors have evolved from X-ray film and point diffractometry to area gas-proportional counters, to image plates, and now to CCD detectors. Two new X-ray detector technologies are on the horizon. One is based on the large-area amorphous semiconductors and thin-film transistor arrays which are being intensively developed by many large companies for medical radiography (reviewed by Moy, 1999). The radiographic need is to be able to cover very large areas (*e.g.* 0.5 m^2) with a high-spatial-resolution detector that is sensitive to hard X-rays. A number of these detectors are at the moment (1999) poised for introduction, but they are specialized for radiographic applications and are poorly suited for relatively long, low-noise integration of low-energy X-rays. It remains to be seen whether the technology will succeed and whether it can be modified for quantitative crystallographic applications.

A second technology being developed specifically for quantitative X-ray diffraction is based on solid-state pixel array detectors (PADs) (Iles *et al.*, 1996; Datte *et al.*, 1999; Barna *et al.*, 1997; Rossi *et al.*, 1999). In a PAD, X-rays are stopped directly in a semiconductor and the resulting signal is processed by electronics integrated into each pixel. Direct conversion of X-rays into electrical signals in a high-grade semiconductor has many advantages: many signal electrons are produced for each X-ray, and the conversion medium is very linear, has low noise and is well understood. Since each pixel has its own electronics, there is enormous flexibility in performing local signal processing. In principle, PADs have tremendous advantages of sensitivity, flexibility, noise and stability. The challenge will be to make PADs of a size and format useful for crystallography, while still being sufficiently affordable to be commercially viable.

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