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7.1. Detectors for X-rays

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7.1.1. Photographic film*

In 1962, when Volume III of *International Tables for X-ray Crystallography* was published, photographic film was the commonest detector for X-rays. Now it has been largely supplanted by the electronic devices described in other sections, but it is still much used in powder cameras and in preliminary investigation of specimens.

X-rays and other radiations cause blackening of silver halide emulsions, and their intensity can be measured accordingly. The blackening of the film is expressed in units of density:

$$D = \log_{10} (\mathscr{I}_{\rm incident}/\mathscr{I}_{\rm transmitted}), \qquad (7.1.1.1)$$

where $\mathscr{I}$ refers to the intensity of the ordinary light incident on the film. Measured densities must be corrected by subtracting the fog density D_F measured on a non-exposed part of the film.

Important features of the photographic process for strongly ionizing radiations such as X-rays and electrons are:

(i) For a given total exposure E the relationship between D and E is, to a close approximation, independent of the time variation of the intensity of the incident radiation. It does not matter whether the X-ray quanta arrive continuously or in short intense bursts (Mees, 1954).

(ii) The density D increases linearly with E up to $D \simeq 1$, then increases more slowly.

Photographic intensity measurements may be made either visually or by using a microdensitometer.

7.1.1.1. *Visual estimation*

Visual estimation consists of comparing the spot or line to be measured with a series of exposure-calibrated marks similar in shape to the object of measurement, and preferably made with the same specimen and incident beam. Lack of complete similarity and unfavourable background usually cause the error of such measurements to be larger than the optimum contrast threshold of the eye. For a spot area of 1 mm^2, the latter amounts to roughly 1% or 0.004 density units, a difference that can in fact be detected under favourable circumstances (low density and low background).

7.1.1.2. *Densitometry*

If the blackening is measured with a microdensitometer, an accuracy of 0.002 density units up to densities of at least 2 is easily attained. Higher precision is rarely required, as the limiting factors are graininess of the film and irregularities in the emulsion and processing. The grains in processed X-ray film are larger than those produced by visible light, and occur in clusters around each absorbed quantum. The resulting statistical fluctuations may be minimized by appropriate choice of densitometer slit dimensions and scanning speed. If the X-rays are not incident normally on double-coated film, it may be necessary to make corrections for obliquity (Whittaker, 1953; Hellner, 1954).

* Editorial condensation of the entry by P. M. de Wolff in Chapter 3.1 of Volume III.

7.1.2. Geiger counters†

Geiger-Müller counters (Geiger & Müller, 1928) are now obsolete for data collection, but are still used in portable monitors for X-rays. A cross section of a once-popular type is shown in Fig. 7.1.2.1(*a*). The cathode C is a cylinder made of a metal such as chrome-iron, about 2 cm in diameter and 10 cm long. The anode A is a tungsten wire about 0.7 mm in diameter mounted coaxially with C and terminated by a bead to prevent destructive electrical discharges from its tip. About 1400 V DC is applied between C and A. X-rays enter at a low-absorption end window W, made of mica about 0.013 mm thick or other suitable material; beryllium would now be used. The gas filling may be argon at a pressure of about 55 cm Hg or krypton at a lower pressure. A small amount of halogen (~0.4% of chlorine or bromine) helps to avoid destructive discharges. Separating the anode and the window is a dead space in which X-rays are absorbed but not detected.

The quantum-counting efficiency varies with wavelength; for Cu K and its neighbours, it is about 50% and, for Mo K, it is about 10%. For the longer wavelengths, it is limited by absorption in the window and the dead space, so it is important to keep these as thin as practicable. For the shorter wavelengths, it is limited by the transparency of the gas in the sensitive volume.

† Editorial condensation of the entry by W. Parrish in Chapter 3.1 of Volume III. Several papers on the relative advantages of various detectors are collected in Parrish (1962). Sections 7.1.2–7.1.4 have been slightly revised by J. I. Langford.

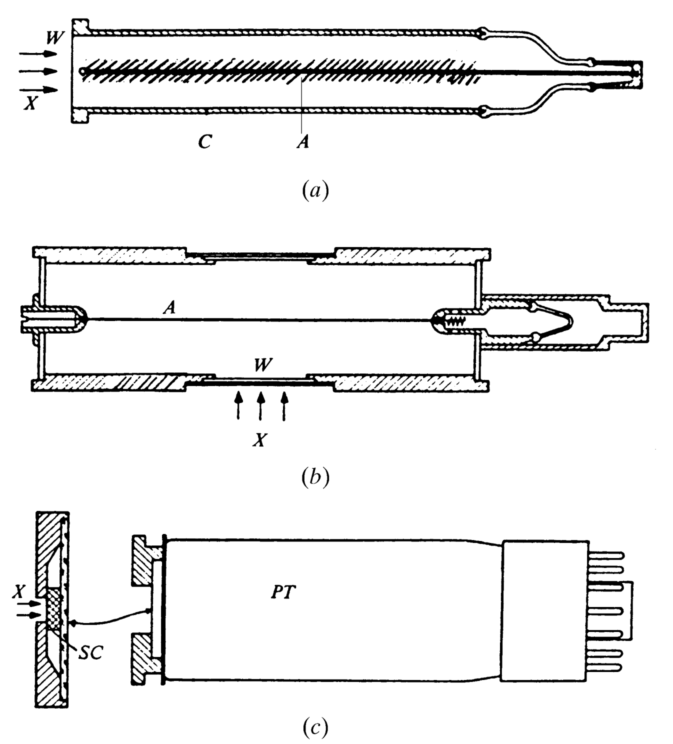

Fig. 7.1.2.1. Detectors used for diffractometry: (*a*) Geiger counter, (*b*) side-window proportional counter, (*c*) end-window scintillation counter. The arrows X show direction of incident X-ray beam, W thin window, C cathode, A anode, SC scintillation crystal, PT photomultiplier tube.

The tube is not uniformly sensitive across its diameter. The maximum sensitivity is confined to the cylindrical volume shown cross-hatched in the figure. The diameter of this sensitive area depends on the gas filling and the geometry of the tube. For maximum efficiency, the X-ray beam should be directed along and close to the anode, but should not strike it. Geiger counters are not critically temperature-dependent. Linearity of response is limited by the dead-time following the discharge initiated by the absorption of a quantum and the magnification of the few hundred ions produced to some millions by their acceleration under the electric field. To produce this amplification, a certain minimum threshold voltage is required. Above this minimum, there is a plateau extending for several hundred volts within which the number of quanta detected is essentially independent of the applied voltage and the size of the pulses is essentially independent of the energy of the absorbed quantum.

Geiger counters are simple to use and show little deterioration even after prolonged use. However, since the pulses are all of about the same size, pulse-height discrimination cannot be used, and the long dead-time limits linearity of response unless special monitoring circuits are used (Eastabrook & Hughes, 1953). They have been almost completely superseded by other types of counter, described in Sections 7.1.3.–7.1.8.

7.1.3. Proportional counters (By W. Parrish)

7.1.3.1. *The detector system*

The commonest types of detector for both powder and single-crystal diffractometry are proportional counters and especially scintillation counters (Section 7.1.4). The detector system consists of the detector itself, a high-voltage power supply, a single-channel pulse-height analyser, and a scaling circuit, as shown schematically in Fig. 2.3.3.5. For position-sensitive detectors (Section 7.1.3.3) and solid-state detectors (Sections 7.1.4.2 and 7.1.5), multichannel analysers are necessary. The X-ray manufacturers and a number of electronic companies provide complete detector systems, often integrated with the computer data-collection system.

7.1.3.2. *Proportional counters*

Proportional counters are available in various sizes and gas fillings. A typical detector is a metal cylinder about 2 cm in diameter and 8–10 cm long, with central wire anode and 0.13 mm Be side window, Fig. 7.1.2.1(*b*). Some have an opposite exit window to transmit the unabsorbed beam and thus avoid fluorescence from the wall. The tube may be filled with Xe to atmospheric pressure for high absorption, and a small amount of quenching gas such as CO_2 or CH_4 is added to limit the discharge. When an X-ray quantum is absorbed, the discharge current is the sum of the Townsend avalanches of the secondary electrons and the gas amplification is about 10^4. A charge-sensitive preamplifier is generally used. Some proportional counters are filled to several atmospheres pressure to increase the gas absorption. Very thin organic film windows are used for very long wavelengths as in fluorescence spectroscopy. They may transmit moisture, and gas may migrate through them so that flow counters are used to replenish the gas. This requires careful control of the pressure to avoid changes in the counting efficiency.

7.1.3.3. *Position-sensitive detectors*

One variety of position-sensitive detector, in which the photon absorptions in different regions are counted separately, is a special type of proportional counter. The following description applies primarily to one-dimensional detectors for powder diffractometry; two-dimensional (area) detectors are treated in Section 7.1.6.

Position-sensitive detectors (PSD's) are being used in increasing number for various powder-diffraction studies. They have the great advantage of simultaneously recording a much larger region of the pattern than conventional counters. The difference in receiving apertures determines the gain in time. The position at which each quantum is detected is determined electronically by the system computer and stored in a multi-channel analyser. There is a digital addition of each incident photon address and the angular address of the diffractometer.

The PSD's are available in short straight form and as longer detectors with curvature to match the diffractometer focusing circle. The short detectors can be used in a stationary position to cover a small angular range or scanned. Göbel (1982) developed a high-speed method using a short (8° window) scanning PSD with 50 µm linear resolution in the diffractometer geometry shown in Fig. 2.3.1.12(*b*). He was able to record at speeds of a hundred or more degrees a minute, and patterns with reasonably good statistical precision in several tens of degrees a minute. This is faster than conventional energy-dispersive diffraction and has the advantage of much higher resolution.

The PSD should be selected to match best the diffraction geometry. The detector is sensitive across the 1–2 cm gas-absorption path. If the diffracted rays are not perpendicular to the window, the parallax causes broadening and loss of resolution. This becomes important in the focusing geometries and can be minimized if the diffractometer and specimen focusing circles are nearly coincident. A large loss of resolution would occur in the conventional geometry, Fig. 2.3.1.3, because only the central ray of a single reflection would be normal to the window. The problem is minimized in powder-camera geometry with a thin rod specimen, Fig. 2.3.4.1(*a*), where the entire pattern can be recorded with a long, curved PSD (Ballon, Comparat & Pouxe, 1983); see also Shishiguchi, Minato & Hashizume (1986), Lehmann, Christensen, Fjellvåg, Feidenhans'l & Nielsen (1987), Wölfel (1983), and Foster & Wölfel (1988).

7.1.3.4. *Resolution, discrimination, efficiency*

The topics of energy resolution, pulse-height discrimination, quantum-counting efficiency, and linearity are common to proportional, scintillation and solid-state counters, and are treated in Subsections 7.1.4.3.–7.1.4.5.

7.1.4. Scintillation and solid-state detectors (By W. Parrish)

7.1.4.1. *Scintillation counters*

The most frequently used detector is the scintillation counter (Parrish & Kohler, 1956). It has two elements: a fluorescent crystal and a photomultiplier tube, Fig. 7.1.2.1(*c*). For X-ray diffraction, a cleaved single-crystal plate of optically clear NaI activated with about 1% Tl in solid solution is used. The crystal is hygroscopic and is hermetically sealed in a holder with thin Be entrance window and glass back to transmit the visible-light scintillations. The size and shape of the crystal can be selected, but is usually a 2 cm diameter disc or a rectangle $20 \times 4 \times 1$ mm thick. A small thin crystal has been used to reduce the background from radioactive samples (Kohler & Parrish, 1955). A viscous mounting fluid with about the same refractive index as the glass is used to reduce light reflection and to attach it to the end of the photomultiplier tube. The crystal and

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