

2. INSTRUMENTATION AND SAMPLE PREPARATION

energy range of a detector. The DQE drops significantly if a detector is used out of its energy range. For instance, the energy range of MWPC and microgap detectors is about 3 to 15 keV. The DQE with Cu $K\alpha$ radiation (8.06 keV) is about 80%, but drops gradually when approaching the lower or higher energy limits. The energy range of imaging plates is much wider (4–48 keV). The energy range of a CCD, depending on the phosphor, covers from 5 keV up to the hard X-ray region.

2.5.3.2.4. Detection limit and dynamic range

The detection limit is the lowest number of counts that can be distinguished from the absence of true counts within a specified confidence level. The detection limit is estimated from the mean of the noise, the standard deviation of the noise and some confidence factor. In order to have the incoming X-ray photons counted with a reasonable statistical certainty, the counts produced by the X-ray photons should be above the detector background-noise counts.

The dynamic range is defined as the range extending from the detection limit to the maximum count measured in the same length of counting time. The linear dynamic range is the dynamic range within which the maximum counts are collected within the specified linearity. For X-ray detectors, the dynamic range most often refers to linear dynamic range, since only a diffraction pattern collected within the linear dynamic range can be correctly interpreted and analysed. When the detection limit in count rate approaches the noise rate at extended counting time, the dynamic range can be approximated by the ratio of the maximum count rate to the noise rate.

Dynamic range is very often confused with the maximum count rate, but must be distinguished. With a low noise rate, a detector can achieve a dynamic range much higher than its count rate. For example, if a detector has a maximum linear count rate of 10^5 s^{-1} with a noise rate of 10^{-3} s^{-1} , the dynamic range can approach 10^8 for an extended measurement time. The dynamic range for a 2D detector has the same definition as for a point detector, except that with a 2D detector the whole dynamic range extending from the detection limit to the maximum count can be observed from different pixels simultaneously. In order to record the entire two-dimensional diffraction pattern, it is necessary for the dynamic range of the detector to be at least the dynamic range of the diffraction pattern, which is typically in the range 10^2 to 10^6 for most applications. If the range of reflection intensities exceeds the dynamic range of the detector, then the detector will either saturate or have low-intensity patterns truncated. Therefore, it is desirable that the detector has as large a dynamic range as possible.

2.5.3.2.5. Types of 2D detectors

2D detectors can be classified into two broad categories: photon-counting detectors and integrating detectors (Lewis, 1994). Photon-counting area detectors can detect a single X-ray photon entering the active area. In a photon-counting detector, each X-ray photon is absorbed and converted to an electrical pulse. The number of pulses counted per unit time is proportional to the incident X-ray flux. Photon-counting detectors typically have high counting efficiency, approaching 100% at low count rate. The most commonly used photon-counting 2D detectors include MWPCs, Si-pixel arrays and microgap detectors. Integrating area detectors, also referred to as analogue X-ray imagers, record the X-ray intensity by measuring the analogue electrical signals converted from the incoming X-ray flux. The

signal size of each pixel is proportional to the fluence of incident X-rays. The most commonly used integrating 2D detectors include image plates (IPs) and charge-coupled devices (CCDs).

The selection of an appropriate 2D detector depends on the X-ray diffraction application, the sample condition and the X-ray beam intensity. In addition to geometry features, such as the active area and pixel format, the most important performance characteristics of a detector are its sensitivity, dynamic range, spatial resolution and background noise. The detector type, either photon-counting or integrating, also leads to important differences in performance. Photon-counting 2D detectors typically have high counting efficiency at low count rate, while integrating 2D detectors are not so efficient at low count rate because of the relatively high noise background. An MWPC has a high DQE of about 0.8 when exposed to incoming local fluence from single photons up to about $10^3 \text{ photons s}^{-1} \text{ mm}^{-2}$. The diffracted X-ray intensities from a polycrystalline or powder sample with a typical laboratory X-ray source fall into this fluence range. This is especially true with microdiffraction, where high sensitivity and low noise are crucial to reveal the weak diffraction pattern. Owing to the counting losses at a high count rate, the DQE of an MWPC decreases with increasing count rate and quickly saturates above $10^3 \text{ photons s}^{-1} \text{ mm}^{-2}$. Therefore, an MWPC is not suitable for collecting strong diffraction patterns or for use with high intensity sources, such as synchrotron X-ray sources. An IP can be used in a large fluence range from $10 \text{ photons s}^{-1} \text{ mm}^{-2}$ and up with a DQE of 0.2 or lower. An IP is suitable for strong diffraction from single crystals with high-intensity X-ray sources, such as a rotating-anode generator or synchrotron X-ray source. With weak diffraction signals, the image plate cannot resolve the diffraction data near the noise floor. A CCD detector can also be used over a large X-ray fluence range from $10 \text{ photons s}^{-1} \text{ mm}^{-2}$ to very high fluence with a much higher DQE of 0.7 or higher. It is suitable for collecting diffraction of medium to strong intensity from single-crystal or polycrystalline samples. Owing to the relatively high sensitivity and high local count rate, CCDs can be used in systems with either sealed-tube X-ray sources, rotating-anode generators or synchrotron X-ray sources. With a low DQE at low fluence and the presence of dark-current noise, a CCD is not a good choice for applications with weak diffraction signals. A microgap detector has the best combination of high DQE, low noise and high count rate. It has a DQE of about 0.8 at an X-ray fluence from single photons up to about $10^5 \text{ photons s}^{-1} \text{ mm}^2$. It is suitable for microdiffraction when high sensitivity and low noise are crucial to reveal weak diffraction patterns. It can also handle high X-ray fluence from strong diffraction patterns or be used with high-intensity sources, such as rotating-anode generators or synchrotron X-ray sources.

2.5.3.3. Data corrections and integration

2D diffraction patterns contain abundant information. In order to interpret and analyse 2D patterns accurately it is necessary to apply some data-treatment processes (Sulyanov *et al.*, 1994; Scheidegger *et al.*, 2000; Cervellino *et al.*, 2006; Boesecke, 2007; Rowe, 2009). Most data-treatment processes can be categorized as having one of the following four purposes: to eliminate or reduce errors caused by detector defects; to remove undesirable effects of instrument and sample geometry; to transfer a 2D frame into a format such that the data can be presented or further analysed by conventional means and software; and cosmetic treatment, such as smoothing a frame for reports and publications.

2.5. TWO-DIMENSIONAL POWDER DIFFRACTION

2.5.3.3.1. Nonuniform response correction

A 2D detector can be considered as an array of point detectors. Each pixel may have its own response, and thus a 2D detector may exhibit some nonuniformity in intensity measurement when exposed to an isotropic source. The nonuniform response can be caused by manufacturing defects, inadequate design or limitations of the detector technology. For instance, a nonuniform phosphor screen or coupling fibre optic for a CCD detector may cause nonuniformity in quantum efficiency (Tate *et al.*, 1995). A gas-filled detector may have a different intensity response between the detector edge and centre due to the variation in the electric field from the centre to the edge. A thorough correction to the nonuniformity of the intensity response can be performed if the detector counting curves of all pixels are given. In practice, this is extremely difficult or impossible, because the behaviour of a pixel may be affected by the condition of the adjacent pixels and the whole detector. The practical way to correct the non-uniformity of the intensity response is to collect an X-ray image from an isotropic point source at the instrument centre and use the image data frame to generate a correction table for the future diffraction frames. The frame collected with the isotropic source is commonly referred to as a 'flood-field' frame or a flat-field image, and the correction is also called a flood-field correction or flat-field correction (Stanton *et al.*, 1992). Another type of correction for a nonuniform response is background correction. Background correction is done by subtracting a background frame from the data frame. The background frame is collected without X-ray exposure. Integrating detectors, such as image plates or CCDs, have a strong background which must be considered in nonuniform response correction. Photon-counting detectors, such as MWPC and microgap detectors, have negligible background, so background correction is not necessary.

The X-ray source for calibration for flood-field correction should be a uniform, spherically radiating point source. Identical brightness should be observed at any pixel on the detector. The radiation strength of the source should match the intensity of the diffraction data to be collected. The photon energy of the source should be the same as or close to the X-ray beam used for diffraction-data collection so that the detector behaves the same way during calibration and data collection.

There are many choices of calibration sources, including X-ray tubes, radioactive sources, diffuse scattering or X-ray fluorescence. The radioactive source Fe-55 (^{55}Fe) is the most commonly used calibration source for a diffraction system because of its major photon energy level of 5.9 keV. X-ray fluorescence is an alternative to a radioactive source. Fluorescence emission is generated by placing a fluorescent material into the X-ray beam. Fluorescence radiation is an isotropic point source if the irradiated area is a small point-like area. For example, Cu $K\alpha$ can produce intense fluorescence from materials containing significant amounts of iron or cobalt and Mo $K\alpha$ can produce intense fluorescence from materials containing yttrium. In order to avoid a high localized intensity contribution from X-ray diffraction, the fluorescent material should be amorphous, such as a glassy iron foil. An alternative to a glassy alloy foil is amorphous lithium borate glass doped with the selected fluorescent element up to a 10% concentration (Moy *et al.*, 1996).

There are many algorithms available for flood-field correction depending on the nature of the 2D detector. The correction is based on the flood-field frame collected from the calibration source. The simplest flood-field correction is to normalize the counts of all pixels to the same level assuming that all pixels have

the same response curve. The corrected frame from an isotropic source is not flat, but maintains the $\cos^3 \phi$ falloff effect, which will be considered in the frame integration. For gas-filled detectors, such as MWPC and microgap detectors, the pixel intensity response is not independent, but is affected by X-ray exposure to surrounding pixels and the whole detector. Flood-field correction is carried out by applying a normalization factor to each pixel in which a 'rubber-sheet' kind of stretching and shrinking in regions along the x and y detector axes slightly alters the size of each pixel (He, 2009). The total number of counts remains the same after the correction but is redistributed throughout the pixels so that the image from an isotropic source is uniformly distributed across the detector. The flood-field calibration must be done with the same sample-to-detector distance as for the diffraction-data collection.

2.5.3.3.2. Spatial correction

In an ideal flat 2D detector, not only does each pixel have the same intensity response, but also an accurate position. The pixels are aligned in the x and y directions with equal spacing. In most cases we assume that the detective area is completely filled by pixels, so the distance between two neighbouring pixels is equivalent to the pixel size. The deviation from this perfect pixel array is called spatial distortion. The extent of spatial distortion is dependent on the nature and limitation of the detector technology. A CCD detector with 1:1 demagnification may have a negligible spatial distortion, but the barrel distortion in the coupling fibre-optic taper can introduce substantial spatial distortion. An image-plate system may have spatial distortion caused by imperfections in the scanning system (Campbell *et al.*, 1995). MWPC detectors typically exhibit more severe spatial distortion due to the window curvature and imperfections in the wire anode (Derewenda & Helliwell, 1989).

The spatial distortion is measured from X-ray images collected with a uniformly radiating point source positioned at the instrument centre and a fiducial plate fastened to the front surface of the detector. The source for spatial correction should have a very accurate position, point-like shape and small size. The fiducial plate is a metal plate with accurately distributed pinholes in the x and y directions. The X-ray image collected with this setup contains sharp peaks corresponding to the pinhole pattern of the fiducial plate. Since accurate positions of the peaks are given by the fiducial plate, the spatially corrected image is a projection of the collected image to this plane. Therefore, the detector plane is defined as the contacting plane between the fiducial plate and detector front face.

Spatial correction restores the spatially distorted diffraction frame into a frame with correct pixel positions. Many algorithms have been suggested for spatial correction (Sulyanov *et al.*, 1994; Tate *et al.*, 1995; Stanton *et al.*, 1992; Campbell *et al.*, 1995). In the spatially corrected frame each pixel is generated by computing the pixel count from the corresponding pixels based on a spatial-correction look-up table. In a typical spatial-correction process, an image containing the spots from the calibration source passing through the fiducial plate is collected. The distortion of the image is revealed by the fiducial spots. Based on the known positions of the corresponding pinholes in the fiducial plate, the distortion of each fiducial spot can be determined. The spatial correction for all pixels can be calculated and stored as a look-up table. Assuming that the detector behaves the same way in the real diffraction-data collection, the look-up table generated from the fiducial image can then be applied to the real diffraction frames.