A Comparison of Detectors Used For Microdiffraction Applications.
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Abstract
X-ray diffraction of small particles has been utilized since the introduction of the Debye-Scherrer powder camera in 1916. The evolution of microdiffraction, to arrive at the state of the art, has followed a path that includes various diffractometer methods as well as film methods. In this paper we discuss the evolution of the detectors employed by microdiffraction with an emphasis on the more modern instrumentation. We discuss advantages and disadvantages of one-dimensional detectors such as position sensitive proportional counters and of two-dimensional detectors such as image plates, area detectors and CCDs. These factors are necessary to consider when selecting a microdiffraction method and are based on what is required from the analyses.

Introduction
Analyses of small particles or of areas less than about a millimeter in diameter has been a challenge since the introduction of x-ray diffraction. Many novel methods have been devised using Debye-Scherrer cameras, introduced in 1916, and powder diffractometers since their introduction in the early 1940s [1, 2]. The earliest Debye-Scherrer methods were performed by collimating the X-ray beam to about a millimeter in diameter and analyzing a particle mounted on the end of a fiber. The detector used was a strip of 35mm x-ray photographic film cut to a length equal to the circumference of the camera. The usefulness, from a microdiffraction standpoint, was limited by effects from large crystallite size and preferred orientation of the sample. The Debye Scherrer method was greatly improved with the introduction of the Gandolfi camera in the mid 1960s [1, 2]. The first general purpose camera which collimated the X-ray beam to less than 0.1 mm (100 microns) arrived in 1947 with the introduction of the Chesley microcamera. This instrument had the advantage of using a piece of sheet film as a two-dimensional detector to minimize lost diffraction data due to preferred orientation effects [3, 4]. Microdiffractometer instrumentation using pinhole and total-reflection collimators were introduced in the mid 1970s [5, 6]. The initial version was based on a symmetric powder diffractometer and employed a scintillation detector [6]. The next generation of microdiffractometer had an unusual geometry, was difficult to align, and resulted in data that were difficult to interpret [6, 7]. A later asymmetric diffractometer method using position sensitive proportional counters was introduced in the late 1980s [5, 6, 7]. Several research facilities and industrial applications laboratories have modified these types of microdiffraction instruments to employ image plates, position sensitive area detectors, and CCD detectors [8, 9].

Factors to consider
Any one who has worked with x-ray film methods is familiar with the effects of sample selection and preparation on diffraction data. Many journal publications and texts have discussed these effects in detail [1, 2, 4]. In the perfect world with the perfect unstrained, fine grained sample with no preferential orientation, the diffraction rings will be perfectly spherical with sharp lines.
Increased grain size will produce spotty rings. Preferential orientation will produce broken rings. Both of these effects are graphically shown throughout this paper. It is easy to envision that the process of collimating a beam to 100μm or less has the same effects on the diffraction data. These are demonstrated in Figure 1 where Wicks et al. used a Norelco microcamera [4], which is similar to the Chesley microcamera [3], in order to study serpentine deposits. The microcamera has the advantage of using a piece of sheet film to obtain data for entire diffraction rings. When the entire ring is collected the effects from orientation and grain size can be observed.

In the early 1970s we used a Gandolfi camera to collect diffraction patterns from single grains or very small amounts of powder. The Gandolfi camera used a method by which the sample is placed on the end of a fiber. Two axes of rotation [2] were used to smooth out the effects from crystallite size and preferred orientation. Data was collected using 35mm film just as with the Debye-Scherrer camera. The advantage this method has is it allows collection of nearly the full

Figure 1. a and b show the Norelco microcamera. C shows diffraction patterns displaying spotty and broken rings caused by crystallite size effects and preferred orientation [4].
possible range of two-theta values as opposed to the limited range in the microcamera which is generally less than about 40° two-theta. This is important to consider if phase identification is the principal information required from the diffraction data.

Diffractometer methods
In the early 1970s Rigaku Corporation started the process of developing a commercially available microdiffractometer. Previous to this, diffractionists would collimate the incident beam from a standard diffractometer to less than a millimeter or so by using collimators or crossed slits. These methods were marginally effective. When Rigaku started their endeavor they tried various detector configurations in order to obtain the best possible balance of two-theta range while minimizing the effects from orientation and crystallite size. The description of the early Rigaku configurations are described by several authors [5,6,7]. P. DeHaven from IBM used a diffractometer that employed a horizontal diffractometer and a scintillation detector [6]. He and others from IBM also used an unusual design shown in Figure 2 [7] which used a scintillation detector to collect diffraction data in the front reflection region and a ring shaped gas-filled proportional counter to collect data in the back reflection region. The detectors were moved along an axis to collect data from a large two-theta range. The detector configuration allowed for the collection of entire diffraction rings. Another advantage of this instrument was the ability to analyze samples in-situ and that strain analyses could be done because of the ability to collect data from the higher two theta regions. This method had the disadvantage of having to merge data from two different types of detectors.

A later method, developed by Rigaku, employed a Gandolfi type configuration. Crystallite size and orientation effects were accounted for by rotating the sample through three axes of rotation. The detector used was a position sensitive proportional counter (PSPC) with a two-theta range of nearly 150°. This diffractometer is shown in Figure 3 [5,10].
Figure 3. Rigaku microdiffractometer which employs a wide angle position sensitive proportional counter and a Gandolfi-like sample motion [7,10].

Basically the position sensitive proportional counter is a gas-filled proportional counter that uses a thin anode wire with collection and pulse counting electronics on both ends. The counting-gas is usually a mixture of 90% argon and 10% methane. Quantum efficiency is increased by flowing the gas under pressure [11]. The diffracted beam passes through a window and releases an avalanche of electrons from the counting gas which strikes the anode wire. A schematic is shown in Figure 4. Poorly conducting anode wires such as molybdenum or platinum are used to slow down the electrons. Two-theta is determined by correlating the rise time on both sides of the wire with the position that the electron avalanche strikes the wire. The spatial resolution on the wire is generally within about 100μm. Two-theta resolution depends on the distance from the sample to the detector.

The advantage of the PSPC is the fact that a large range of two-theta can be collected simultaneously. Also PSPCs have been shown to have very rapid data collection speeds [11]. We have collected excellent diffraction patterns with this type of microdiffractometer when using powders and allowing the sample stage to rotate in all axes. The disadvantages come when less than ideal samples are analyzed. If the situation exists where the sample cannot be rotated, all of the factors discussed earlier can come into play. It is easy to imagine that if a spotty or broken diffraction ring were produced, the thin anode wire from the PSPC can miss a large fraction of the diffracted data. To observe this the reader can draw a thin line through some of the diffraction patterns shown in Figure 1b.
Figure 4. Schematic of a simple position sensitive proportional counter.

Two-dimensional detectors
In order to overcome the limitations of one-dimensional detectors such as the PSPC or scintillation detectors, some diffractionists have modified diffractometers with two-dimensional detectors. These include storage phosphors (image plates), area detectors, and charge coupled devices (CCD) [8,9].

Storage phosphors or image plates can be used essentially anywhere x-ray film can be used. It is based on the use of europium-doped BaBrF grains in place of silver halide, used by photographic paper, as the detecting medium. The BaBrF:Eu$^{2+}$ grains are coated with a binder onto a flexible polyester film base. Basically when the diffracted x-rays hit the storage phosphor the Eu$^{2+}$ turns to Eu$^{3+}$ and the electron goes to the conduction band and is trapped in a Br-F center. The diffraction image is now a latent image similar to that found in a silver halide based film. Scanning the storage phosphor with a red laser causes the trapped electron to be released and a blue photon is emitted from the phosphor. The positions of the blue photons are stored and can be captured by a scanner specifically designed for image plate detectors. The final image is a computer file that can be either observed as diffraction rings or converted to an intensity vs. two-theta plot. Image plates have been used for powder diffraction work as well as texture analyses as shown in Figure 5. The advantage of this detector is that it can be used anywhere film can be used, it is flexible, the image plates can be reused and it does not require the chemicals to develop the film as is the case with photographic film methods. The disadvantage is that it has slightly less resolution than photographic film methods.
Another type of two-dimensional detector being used in microdiffraction by these authors is an area detector. These are also known as multi-wire position sensitive proportional detectors. Typically they have a 512 X 512 wire configuration and they detect x-rays in much the same way as the PSPC described earlier. These units are often filled with a mixture of xenon gas and methane, and the unit is sealed. The xenon mixture has a higher counting efficiency than the argon mixture [11]. The detector's active area can be about 10cm. The final diffraction image is a digital file that can be displayed in an x-y format and converted to an intensity vs. two-theta plot. The resolution is much the same as with the PSPC. Resolution can be enhanced via software methods by extrapolating between the wires thus creating a pseudo 1024 X 1024 set of wires. Two-theta range can be severely limited by the sample to detector distance. An example of the value of this kind of detector system is shown in the study of a textured ferroelectric memory device presented in Figure 6.

Figure 6. a. is an area detector based microdiffractometer built on a Siemens D-5000 diffractometer. b. is an image of a textured ferroelectric memory device. Partial diffraction rings give the appearance of a pumpkin face.
Another type of two-dimensional detector is the charge coupled device or CCD that is similar to those employed in single crystal systems. A schematic of a CCD is shown in Figure 7. Basically it works by using a fluorescent screen or phosphor such as Gd$_2$O$_2$S:Tb which emits light when struck by the diffracted x-rays. For a diffraction system the active area of the phosphor can be around 8cm. The visible light is transmitted to a CCD chip via a fiber coupling device made of tapered light pipes. The CCD chip typically has a 1024 X 1024 resolution, although 2048 X 2048 chips are available, but they can be prohibitively expensive. The CCD data is processed via a computer and viewed in real time and converted to an intensity vs. two-theta plot [9]. Two-theta resolution with this system is also determined by the distance from the sample to the phosphor. Resolution can be affected by a small amount of visible light spreading in the phosphor. As with is the case with the area detector, two-theta range is limited by the sample to detector distance.

![Figure 7. CCD detectors work by converting x-rays to visible light using a phosphor or scintillator. The resulting image is transferred to the CCD chip via a fiber coupled device.](image)

**Summary**

There are several detector configurations available by the various x-ray vendors which employ either one-dimensional or two-dimensional detectors. Each have advantages and disadvantages depending on the experimental requirements.

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