## 2.3.4. Powder cameras

The use of powder cameras has greatly diminished in recent years, having been largely replaced by diffractometers. Detailed descriptions of the many types of camera, their use, film measurement, and interpretation have been published in the books by Peiser, Rooksby & Wilson (1955), Azároff & Buerger (1958), Taylor (1961), Alexander (1969), Lipson & Steeple (1970), Klug & Alexander (1974), Cullity (1978), and Barrett & Massalski (1980). The following is an outline of the more important features.

The most commonly used cameras are:

(*a*) Cylindrical camera with narrow fibre-shaped specimen and Straumanis film mounting.

(*b*) Guinier focusing monochromator camera with flat transmission specimen and cylindrical film.

(*c*) Flat-film camera for Laue patterns and crystal orientation.

The best results are obtained using the X-ray tube spot focus for non-focusing methods as in (*a*) and (*c*), and the line focus for focusing cameras as in (*b*). A filter is used to eliminate the $K\beta$ lines in the methods that do not use a monochromator. Double-coated film is used for cameras in which the reflections are normal to the film. Single-coated film is used for focusing cameras; alternatively, double-coated film can be used if the second image is prevented from developing (Parrish, 1955).

In all film methods, it is necessary to account for film shrinkage in the development processing to obtain correct angle measurements. In the Straumanis film mounting, Fig. 2.3.4.1(*a*), the arcs can be measured around the incident and exit holes to obtain a linear measure of the effective camera diameter, *i.e.* $180^\circ 2\theta$. Other methods include exposing a transparent scale on the film prior to development, installing a pair of knife edges with accurately measured separation just above the film to cast sharp images on both ends of the film, or incorporating a standard material in the specimen. Exposure times vary from a few minutes to an hour or more depending on the specimen and the various camera parameters.

### 2.3.4.1. *Cylindrical cameras (Debye–Scherrer)*

The design of cylindrical powder cameras with Straumanis film mounting was described by Buerger (1945) and the collimators by Parrish & Cisney (1948). Straumanis developed the method to an art and used it to measure lattice parameters, thermal expansion, and other properties of many materials; see, for example, Straumanis (1959), which contains references to many of his papers. In the USA, the camera diameter was usually made 57.3 or 114.6 mm to simplify measuring the film with a millimetre scale, 1 mm = $1^\circ$ or $2^\circ 2\theta$. One of the major advantages of the method is that the full reflection range is recorded simultaneously on the film. Other advantages are that the effects of preferred orientation are immediately apparent on a film, lines can have non-uniform intensity ('spottiness') owing to size effects or there can be broadening owing to structural imperfections. These visual effects, which are less evident with diffractometer data, can be valuable aids in identifying a mixture of substances.

The camera is basically a cylindrical light-tight metal body with removable cover, and the film is pressed around the inside circumference. The beam is defined by an entrance collimator and the undiffracted portion is conducted out by an exit tube; both are mounted on the central plane of the camera and extend inside nearly to the specimen. The specimen is centred and rotated continuously during the exposure; translation may be added to bring more particles into the beam. Evacuating the camera or filling it with helium removes the air scattering which darkens the film in the vicinity of the $0^\circ$ hole.

If the specimen is too thick or has high absorption, the forward reflection lines split because the beam penetrates only the top and bottom of the rod. The diameter of the rod determines the widths of the lines. The line widths are about twice the diameter of the rod at small $2\theta$'s and decrease with increasing $2\theta$. The absorption causes a systematic error in the positions of the lines, which can be handled with a $\cos^2\theta$ or Nelson–Riley plot (Section 5.2.8). The sample may be small – only about 0.1 mg is required. Axial divergence causes the well known 'umbrella' or 'broom' broadening illustrated in Fig. 2.3.4.1(*b*). It is essential to measure the film along the equator where the lines are narrowest and shifts the smallest. The specimens should be less than 0.5 mm diameter and may be coated on a fine wire or glass fibre (silica or Lindemann glass), or packed into a capillary (commercially available).

Read & Hensler (1972) modified a Debye–Scherrer camera to use flat specimens for thin-film analysis (Tao & Hewett, 1987).

### 2.3.4.2. *Focusing cameras (Guinier)*

The Guinier camera (Guinier, 1937, 1946; Guinier & Dexter, 1963) uses a high-quality asymmetric focusing monochromator and cylindrical camera with a thin transmission specimen, Fig. 2.3.4.1(*c*). The film must be placed at the focal point of the monochromator, which can be adjusted to reflect only the $K\alpha_1$ line. When the camera is in the position shown, the angular range is larger on one side of the film than the other (asymmetric

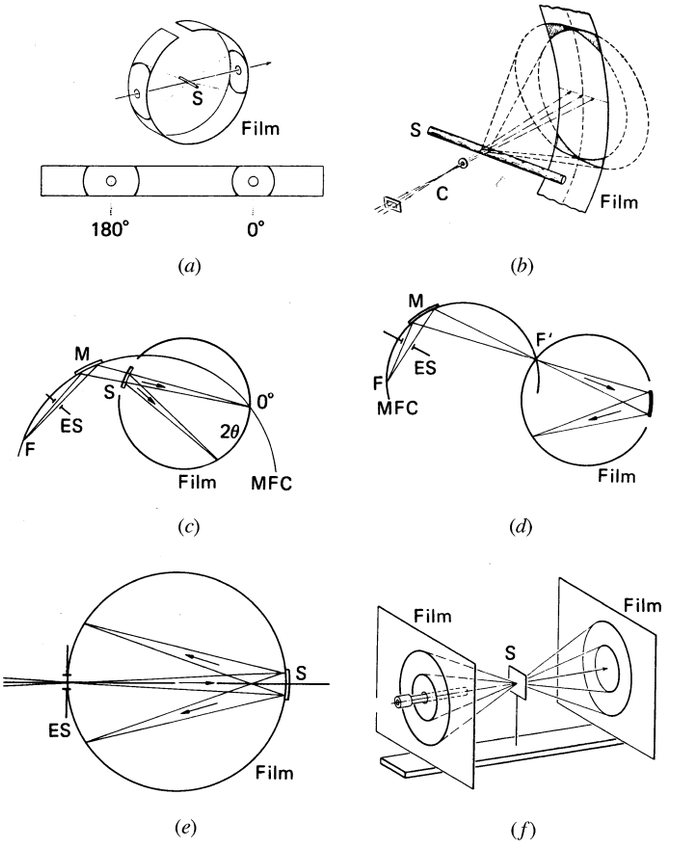


Fig. 2.3.4.1. Powder-camera geometries. (*a*) Straumanis film setting. (*b*) Origin of 'umbrella' effect (axial divergence). (*c*) Guinier camera with specimen in transmission and (*d*) in reflection. (*e*) Symmetrical back-reflection focusing camera. (*f*) Flat-film camera for forward- and back-reflection.



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setting). If the camera is placed so that the rays from the monochromator are along the camera diameter, the angular range is the same on both sides of the 0° point (symmetric setting) and the usable range is about 60°2$\theta$. The sharpest lines are obtained when the rays are nearly normal to the film. The lines are broadened by inclination of the rays to the film, axial divergence, and specimen thickness. The camera can also be used with the specimen in reflection so that it becomes a Seemann–Bohlin camera with only the back reflections accessible [Fig. 2.3.4.1(*d*)]. Hofmann & Jagodzinski (1955) designed a double camera in a single body that can record transmission and reflection patterns on separate films.

de Wolff (1948) described a novel Guinier-type camera that can simultaneously record up to four patterns of different specimens on one film with a single monochromator and long fine-focus X-ray tube. The patterns are separated by horizontal partitions. There are some differences in the line widths in the top and bottom patterns. Malmros & Werner (1973) developed an automated film-measuring densitometer to improve the precision in measuring the Guinier films; see also Sonneveld & Visser (1975).

#### 2.3.4.3. *Miscellaneous camera types*

The symmetrical back-reflection camera, Fig. 2.3.4.1(*e*), is mainly used for lattice-parameter and solid-solution studies because the high reflection angles can be recorded. The specimen can be mounted on a curved holder matching the film curvature to obtain sharp lines and is oscillated during exposure.

The flat-plate camera, Fig. 2.3.4.1(*f*), can be used for forward- or back-reflection. The angular range is small and varies inversely with the specimen-to-film distance. Polaroid film is frequently used. The same method is used for Laue photographs, usually in back-reflection with a goniometer to orient the crystal. The method is often used for fibre and polymer specimens because the entire cone can be recorded (Alexander, 1969).

The Gandolfi (1967) camera produces a powder-like pattern from a tiny single crystal by simultaneous rotation of the crystal around two inclined axes. It is often made as a modification to the cylindrical camera. The crystal may be very small but the pattern is greatly improved by using several crystals. The smoothness of the lines depends on the chance orientation of the crystal with respect to the rotation axes, and the multiplicity of the reflection. The centring of the specimen and the rotation axes must be done precisely. Anderson, Zolensky, Smith, Freeborn & Scheetz (1981) obtained patterns routinely from 5 μm particles in 2–4 d exposure at 40 keV, 20 mA in an evacuated camera; see also Sussieck-Fornefeld & Schmetzer (1987) and Rendle (1983). A high-brilliance microfocus X-ray tube can greatly increase the intensity.

Another type of camera for the same purpose was developed by Parrish & Vajda (1971). The small crystal is mounted on a glass fibre at the end of a vertical shaft that rotates continuously and simultaneously scans about 90°. The film is mounted in a half-cylinder with about 20 mm radius. A microscope is used for precise alignment and centring.

A camera with a wide film cassette has been used for high-temperature diffraction patterns. The cassette can be translated synchronously with the change in temperature, or held in fixed positions during exposure at selected temperatures. The advantage is that all the patterns are recorded on a single film showing the phase changes and thermal expansion as a function of temperature. A Weissenberg camera can be adapted for this purpose.

### 2.3.5. Generation, modifications, and measurement of X-ray spectra

This section covers methods for using X-ray tubes and their operation. The methods of modifying the X-ray spectrum by crystal monochromators, filters, and the detector system apply to powder and single-crystal diffraction. Chapter 4.2 contains a more detailed description of the physics of X-ray sources.

#### 2.3.5.1. *X-ray tubes*

Vacuum-sealed water-cooled X-ray tubes of the type shown in Fig. 2.3.5.1 are almost exclusively used for powder diffraction. They are installed in either a vertical or a horizontal shield (sometimes called a tower) mounted on the generator, or remotely operated with a long high-voltage cable. The shield is designed to seat the tube cap in the correct position, which allows tube replacement without realigning the instruments. Rotating-anode tubes are becoming more popular. They may be operated at higher currents and, although they require continual pumping, recent designs incorporating a ferromagnetic seal and turbomolecular pump make their use virtually as simple as sealed tubes. For additional background information see Phillips (1985) and Yoshimatsu & Kozaki (1977). End-window tubes with large focal spot have been used mainly for X-ray-fluorescence spectroscopy (Arai, Shoji & Omote, 1986), and fine-point-focus tubes for Kossel diagrams.

The maximum permissible power ratings for sealed water-cooled diffraction tubes are about 60 kV, 60 mA and 3 kW. The rating varies with the focal-spot size, anode element, and the particular manufacturer's specifications. Table 2.3.5.1 lists some typical maximum ratings of sealed and rotating-anode tubes. The brightness or specific loading, expressed as watts per square mm, increases with decreasing focal-spot size. There is a very large increase in brightness in the small microfocus sources that

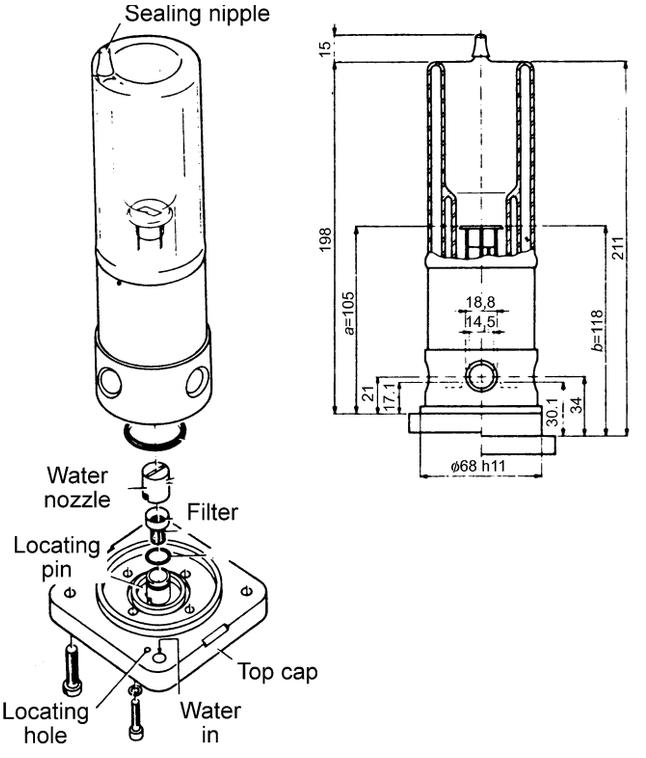


Fig. 2.3.5.1. Sealed X-ray diffraction tube (Philips), dimensions are given in mm. $a$ = 'short' focus, $b$ = 'long' focus.



references