International Tables for Crystallography (2006). Vol. C, Section 3.4.1.2.2, pp. 162–163.

3.4. Mounting and setting of specimens for X-ray crystallographic studies

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3.4.1. Mounting of specimens

3.4.1.1. *Introduction*

This section deals with the mounting of two categories of specimens:

(1) polycrystalline;

(2) single crystal.

Category 2 is further divided into single crystals of small organic and inorganic molecules, and those of biological macromolecules at both ambient and cryogenic temperatures. Commonly used methods of mounting specimens for both camera and diffractometer, and most other detector systems are described.

The bibliography is necessarily selective and wherever possible has been restricted to journals and textbooks that are readily accessible to a crystallographic laboratory. It should also be noted that there exist, worldwide, various centres specializing in synchrotron-radiation and neutron diffraction techniques. Within these centres lies a wealth of experience in sample handling and preparation. For specialist purposes, communication with local contacts at such centres may provide invaluable assistance.

3.4.1.2. *Polycrystalline specimens*

3.4.1.2.1. *General*

Informative accounts of the powder method of recording diffraction patterns have been given by Klug & Alexander (1954), D'Eye & Wait (1960) and Dent Glasser (1977). There are three principal methods of preparing polycrystalline specimens for mounting in powder cameras:

(1) encased;

(2) bonded;

(3) fibre supported.

The most common method of preparing samples of polycrystalline materials is to *encase* them in thin-walled capillary tubes, for Debye–Scherrer camera work, or into sample holders, for Guinier camera and diffractometer measurements. This technique has the advantage that the sample can be readily protected from attack by oxygen, carbon dioxide and water vapour, and, if necessary, the sample preparation can be undertaken in an inert atmosphere (Lange & Haendler, 1972; D'Eye & Wait, 1960). The precise details of sample preparation and mounting will be dependent on the type of camera or diffractometer used, but the particle size should be generally less than 10 μm for stationary samples and diffractometer work. A slightly larger particle size, 45 μm, can be used for Debye–Scherrer camera work if the specimen is rotated. Foit (1982) has described a simple method of filling thin-walled capillaries using an ultrasonic vibrator. A frequent problem affecting intensity measurements from powder specimens is caused by preferred orientation when powder samples are packed or pressed. McMurdie, Morris, Evans, Paretzkin & Wong-Ng (1986) have described a method of sample preparation suitable for a diffractometer that minimizes this problem.

Capillaries made from lithium beryllium borate (Lindemann glass), borosilicate (*e.g.* Pyrex glass), or fused silica are commercially available in a variety of internal diameters. For very high temperatures, thin-walled ceramic or metal capillaries can be used. The diffraction pattern of the metal can be used as an internal standard. Capillaries that are suitable for materials that react with glass can be made from various organic polymers. Table 3.4.1.1 lists details of capillaries and other containers suitable for encasing powder specimens.

In the *bonded* method, the polycrystalline material is mixed with an adhesive such as gum tragacanth or ethyl cellulose, and the mixture is wetted with water or aqueous alcohol to form a viscous paste. The paste is then rolled between two glass slides or extruded through a glass capillary, using a glass or metal piston, to form a cylindrical sample. This can be cut to length and either glued, fixed with plasticine, or cemented (for high-temperature work) to the camera mounting pin. Alternatively, the sample can be compressed and compacted in a die to form a solid rod, or, for diffractometers, into a disc. In the case of very small quantities of material, the powder can be smeared with silicone vacuum grease over the surface of a disc-shaped silica crystal. The silica can then be used as an internal standard.

In the *fibre-supported* method, a silica, Lindemann, or borosilicate glass fibre moistened with adhesive (Canada balsam diluted with xylene, collodion, gum tragacanth and water, dilute fish glue) is dipped into the powder. Experience has shown that powder adhesion to the fibre is often improved if non-drying glues or viscous oils are employed. Hairs of fine organic filaments have been used in place of glass fibres, and for high temperature above 1270° C metal wires are useful. Once again, the metal diffraction patterns can act as internal standards. For extruded metal wires, the wire itself acts as the specimen, and the diameter can be reduced by etching if it is too large, or a glancing-angle diffraction technique can be employed. Various specialized holders for diffraction studies of polycrystalline samples can be found in annual conference proceedings such as EPDIC (*European Powder Diffraction Conference*, Switzerland: Trans Tech Publications) and Advances in X-ray Analysis (*Proceedings of the Annual Conference on the Applications of X-ray Diffraction*, New York/London: Plenum). The journals *Reviews of Scientific Instruments* (American Institute of Physics) and *Nuclear Instruments and Methods* (Elsevier, North-Holland) also provide useful sources of information.

3.4.1.2.2. *Non-ambient conditions*

A number of devices have recently been described to study polycrystalline specimens under non-ambient conditions. Rink, Mathias & Schlenoff (1994) have designed a portable sample housing for work at room temperature with samples that are air or moisture sensitive. A review of designs and desirable features for high-temperature furnaces suitable for X-ray diffractometers has been given by McKinstry (1970). More recently, Puxley, Squire & Bates (1994) have described an *in situ* cell fitted to a Siemens D-500 powder diffractometer that allows samples in flowing or static reactive gas environments at atmospheric pressure and at temperatures up to 1273 K. These authors also review other developments in the field of high-temperature furnaces for polycrystalline X-ray diffraction published since the McKinstry article in 1970. Brown, Swapp, Bennett & Navrotsky (1993) have devised methods to minimize the uncertainties in temperature at the sample and in the position of the sample itself. Tarling, Barnes & Mackay (1984) have adapted a Guinier–Lenné high-temperature powder camera to include a gas rinsing system and a specially designed mini-environment cell in which conditions of industrial furnacing can be simulated. In the neutron area, Lorenz, Neder, Marxreiter, Frey & Schneider

Table 3.4.1.1. *Single-crystal and powder mounting, capillary tubes and other containers*

Material	Temperature range (K)	Comments
(*A*) Capillary tubes		
Glass Lindemann glass Vitreous silica	< 773 < 773 < 1373	Lindemann glass scatters less, but is moisture sensitive Thinner walled tubes that are less sensitive to atmospheric influences can be obtained using other types of glass
Collodion Polyvinyl methylal resin (*e.g.* Formvar) Cellulose acetate	93 to 343 < 323 < 373	These capillaries can be made by coating a copper wire with a solution of the polymer in an appropriate organic solvent. When dry, the metal core may be removed by stretching, to reduce its diameter
Polyethylene	< 373	Tubes may be drawn from the molten polymer using a glass tube and a slow stream of air. The polymer gives a distinct diffraction pattern
(B) Other containers		
Gelatin capsules	< 303	Vessels with very thin, 20 μm, windows can be made
Methyl methacrylate resin (*e.g.* Perspex)	< 338	
Mica	< 1073	Mica windows useful in vessels for small-angle scattering, but the wall size is generally thicker, ∼0.3 mm, and there are discrete lines at 10.00, 3.34 and 2.60 Å in the diffraction pattern
Regenerated cellulose film (*e.g.* cellophane)	Ambient	

For optimum results, tube diameters should be between 0.3 and 0.5 mm with wall thicknesses of 0.02 to 0.05 mm. The materials listed above, except where stated, give diffuse diffraction patterns. If necessary, control diffraction patterns, recorded only from the capillary or other container, should be taken.

(1993) have developed a mirror furnace working at up to 2300 K and suitable for polycrystalline or single-crystal samples.

A comprehensive account of cryogenic studies pertinent to both polycrystalline and single-crystal samples is given by Rudman (1976). Nieman, Evans, Heal & Powell (1984) have described a device for the preparation of low-temperature samples of noxious materials. The device is enclosed in a vanadium can and is therefore only suitable for neutron diffraction studies. Ihringer & Küster (1993) have described a cryostat for powder diffraction, temperature range 8–300 K, for use on a synchrotron-radiation beam line at HASYLAB, Germany (Arnold *et al.*, 1989).

3.4.1.3. *Single crystals (small molecules)*

3.4.1.3.1. *General*

Small single crystals of inorganic and organic materials, suitable for intensity data collection, are normally glued to the end of a glass or vitreous silica fibre, or capillary (Denne, 1971*b*; Stout & Jensen, 1968). A simple device that fits onto a conventional microscope stage to facilitate the procedure of cementing a single crystal to a glass fibre has been constructed by Bretherton & Kennard (1976). The support is in turn fixed to a metal pin that fits onto a goniometer head. For preliminary studies, plasticine or wax are useful fixatives, since it is then relatively easy to alter the orientation of the support, and hence the crystal, as required. For data-collection purposes, the support should be firmly fixed or glued to the goniometer head pin. The fibre should be sufficiently thin to minimize absorption effects but thick enough to form a rigid support. The length of the fibre is usually about 10 mm. Kennard (1994) has described a macroscope that allows specimens to be observed remotely during data collection and can also be used for measurement of crystal faces for absorption correction. Large specimens can be directly mounted onto a camera or onto a specially designed goniometer (Denne, 1971*a*; Shaham, 1982). A method using high-temperature diffusion to bond ductile single crystals to a metal backing, for strain-free mounting, has been described by Black, Burdette & Early (1986).

Prior to crystal mounting, it is always prudent to determine the nature of any spatial constraints that are applicable for the proposed experiment. Some diffractometers have relatively little translational flexibility, and the length of the fibre mount or capillary is critical. For some low-temperature devices where the cooling gas stream is coaxial with the specimen mount, the

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