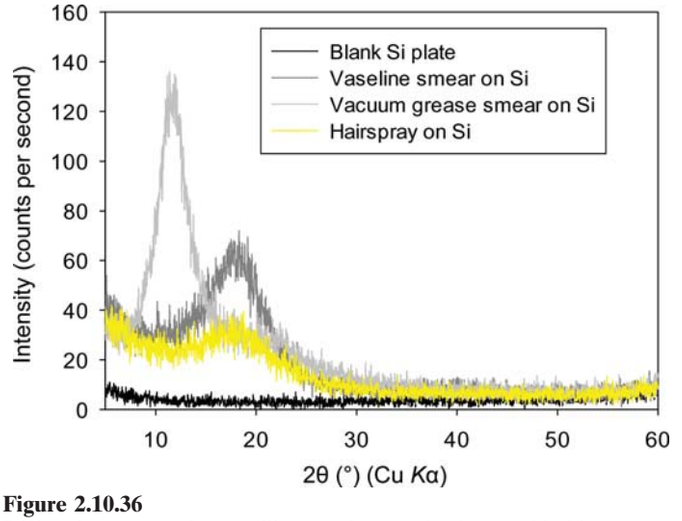

Figure 2.10.36
Diffraction pattern from a silicon-wafer zero-background holder, smears of Vaseline and Corning high-vacuum grease, and the surface treated with hairspray.

of options to find the one with the lowest background and fewest non-Bragg reflections. An unusual alternative is hairspray, which produces a tacky surface when applied correctly whilst having a minimal effect on the resulting diffraction pattern. The medium chosen may also depend on whether the sample must be recovered intact, as contamination with grease might not be acceptable. The effect on the background of different adhesion materials can be seen in Fig. 2.10.36. The Vaseline and vacuum grease smears add broad reflections at approx. 19 and 11° 2θ, respectively, with Cu $K\alpha$ radiation. Where data collection starts above the main portion of the peak the effect may be hardly noticeable, but could be problematic when starting at low 2θ angles. Such broad patterns are straightforward to model with a Debye (diffuse scattering) function, and it is not necessary to subtract them from the raw data.

Should the instrument have parallel-beam geometry, an alternative approach is to use a fixed incident-beam angle, more commonly known as grazing-incidence geometry. In this way the volume of sample illuminated is constant with angle, so in the absence of secondary diffractometer optics the relative intensities will match those expected with conventional geometry. An unfortunate effect of conventional grazing-incidence geometry with long slits is that the peak widths degrade significantly at lower incident angles (Toraya & Yoshino, 1994). It is possible to model the peak broadening in a Rietveld refinement (Rowles & Madsen, 2010) but it is not straightforward. Use of an appropriate secondary optic can avoid the peak-broadening problem but introduces a complex, geometry-dependent intensity correction (Toraya *et al.*, 1993).

2.10.1.4.2. *Transmission sample holders*

Transmission geometry of any type is best suited to samples with low absorption such as organics and polymers, and is preferred for such samples when available. Transmission geometry has advantages when data are required at low diffracting angles. While the beam often has to be stopped-down in reflection geometry to avoid overspilling the sample, this undesired attenuation of the beam is not required for transmission geometry. Another advantage common to both the foil and capillary transmission techniques is that a small quantity of a powdered sample is usually sufficient. Samples small enough to be problematic with reflection geometry will often be perfectly adequate for transmission.

Data collection in transmission geometry is best done with either a parallel-beam or focusing geometry; the focus should be at the detector. Data can be collected using a divergent-beam setup, but the intensities obtained are very low and the resolution is usually poor. Parallel-beam geometry has the advantage that it is able to perform reflection and transmission measurements equally well.

2.10.1.4.2.1. *Flat foils*

Although less commonly used with modern diffractometers, the foil-type transmission sample mounting was quite common in some older-style X-ray cameras. Sprinkling powders onto single-sided Scotch tape was sometimes used with instrumentation such as Hägg–Guinier cameras, but care should be taken as the quality of the tapes as diffraction substrates can vary wildly; the crystallinity of the polymer can be high or low, and the adhesive sometimes contains mineral inclusions, such as talc. In the modern diffractometer, foil-type transmission data can sometimes be collected using the same rotating sample stage as for reflection measurements. Simply turning the stage by 90° and using a different holder can be sufficient if the optical configuration is suitable for both reflection and transmission. For solid organic samples such as polymers this foil transmission geometry has significant advantages because of the lack of transparency effects. It is worth noting, however, that the processing of polymers can induce significant texture, such that the data collected from a film in reflection geometry will not necessarily be identical to those collected in transmission. Should a reproducible pattern independent of geometry be required, then steps should be taken to reduce the sample to a true random powder and/or a 2D detector should be used.

With powder samples the technique requires the use of a transparent substrate, usually in the form of a thin polymer film or foil. In an analytical laboratory the easiest place to find such a substrate is the X-ray fluorescence laboratory, where very thin X-ray transparent polymer films are used for both sample supports and covers for liquid cells. Some of the materials used in these applications are familiar in the diffraction community as windows, *i.e.* Mylar and Kapton, but others such as polypropylene are not. The substrate will obviously add to the background, but a good substrate from a diffraction standpoint combines transparency with a lack of sharp features in the diffraction pattern. This makes fitting the background much easier. Any holder must be capable of stretching or holding the film flat across an opening for the X-ray beam. A commercial version of a foil-type holder is shown prior to assembly in Fig. 2.10.37. Example data from three different XRF films are shown in Fig. 2.10.38, together with that from a thicker Kapton foil commonly used as window material. It is notable that, despite the two 7.6 µm Kapton films being almost twice as thick as the Mylar or polypropylene films, the scattering from them is almost identical. The lack of any distinctive, sharp features above 6° 2θ in the Kapton films makes them attractive in this region, but for low-angle data Mylar is probably the better choice. Although giving a generally higher background, the thicker 50 µm Kapton foils can be used very successfully (see Fig. 2.10.39). Despite the greater attenuation they are much easier to handle, as their greater stiffness and weight makes them less susceptible to static electricity.

One advantage of transmission foil mounts is the small amount of sample required. In a similar way to producing smear mounts

Figure 2.10.37
Parts prior to assembly of a transmission foil sample in the holder. In this instance, micronized quartz is held as a loose powder between two 50 μm Kapton foils while the upper foil is stretched into place by the black clip.

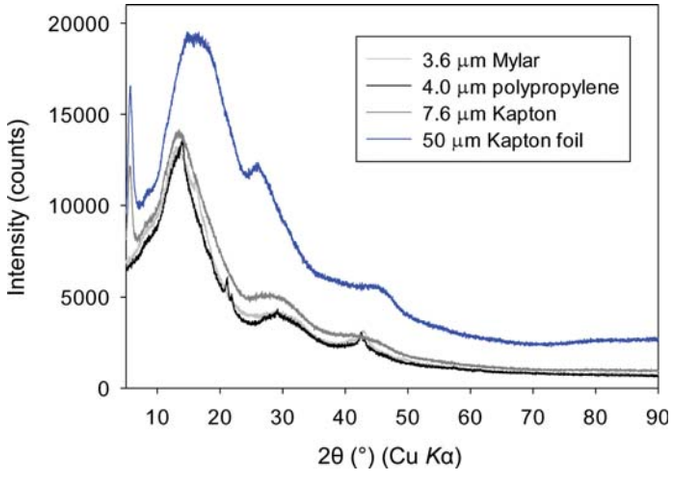

Figure 2.10.38
Transmission data from double layers (as used for powder samples) of different polymer substrate films. They include 3.6 μm Mylar, 4.0 μm polypropylene and 7.6 μm XRF films, and a thicker 50 μm Kapton foil.

for reflection geometry, there are a number of ways to prepare the thin layer required. Loose powders may be trapped between two foils as in Fig. 2.10.39, or alternatively a slurry or smear mount may be used in a similar way to reflection geometry. Although the sample may adhere sufficiently such that a single foil can be used, it may be necessary to use a sandwich in the same way as a loose powder. For instance, slurries do not usually adhere well to Kapton foils, so it is often better to sacrifice a little intensity from the additional Kapton attenuation and ensure the sample does not fall away during data collection. Lack of adhesion could be regarded as an advantage with regards to recovery of valuable samples. Where an adhesive is used, the same considerations as with a smear mount in reflection still apply with regards to background *etc*.

Ideally the sample thickness should be perfectly uniform, but in practice this will rarely be achieved. Commonly a specimen in visible light transmission will appear something like that seen in Fig. 2.10.40. Rotation is used to average out inhomogeneity in the specimen.

Sedimentation during slurry mounting and compression of powders between two foils can lead to preferential orientation

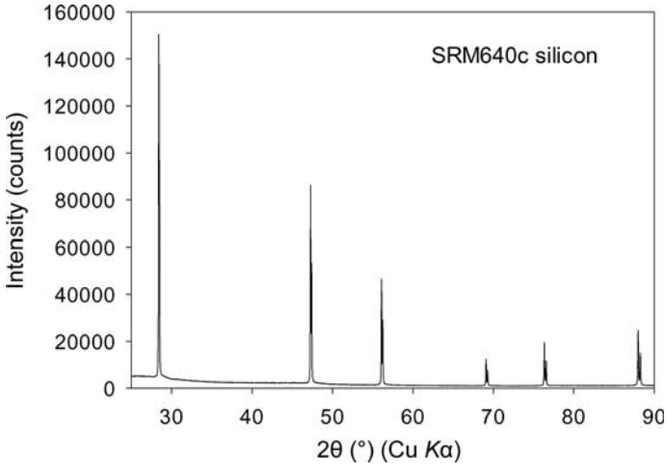

Figure 2.10.39
Diffraction pattern from loose SRM640c powder between two 50 μm Kapton foils.

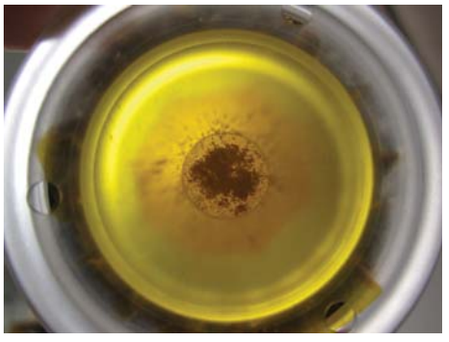

Figure 2.10.40
Transmitted light view of a micronized quartz sample through 50 μm Kapton foils.

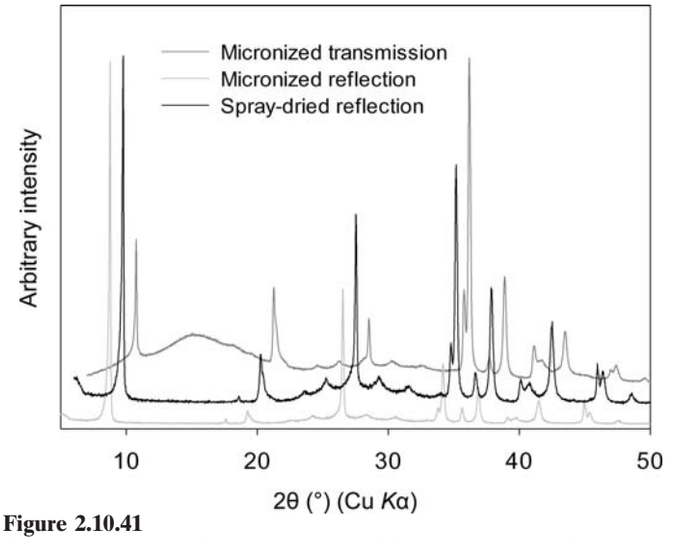

Figure 2.10.41
Comparison of data from micronized 40S mica taken in reflection and transmission geometry, and spray-dried material in reflection geometry. For improved clarity the spray-dried and transmission data sets are translated by +1° and +2° 2θ respectively.

in foil transmission samples just as with flat-plate reflection specimens. Although the physical effect is the same for plate-like crystallites, it should be remembered that the crystallite orientation with respect to the beam is rotated by 90°, so the

resulting diffraction patterns will not look the same. This becomes very apparent when comparing the foil transmission and reflection patterns from the micronized mica in Fig. 2.10.41.

Foil transmission specimens are usually rotated in a similar fashion to a reflection sample, but the improvement in statistics falls short of that found in the capillary geometry described in the next section.

One thing worth considering is that there is an inherent angular intensity aberration due to the plate transmission geometry. Owing to geometrical considerations, the path length through the specimen (and support) increases with angle with a resulting increase in absorption. For refinement work, a $1/\cos\theta$ correction can be applied.

2.10.1.4.2.2. Capillaries

Capillaries are particularly suitable for small samples, air- and moisture-sensitive samples and organics where the absorption is low enough to cause transparency effects in reflection data. They are also commonly used for materials with platy morphologies such as clays to eliminate or greatly reduce preferred-orientation effects. They are less effective at reducing preferred orientation in materials with needle-like morphologies but are still useful, a possible analogy being that the crystallites pack into the capillary like a handful of pencils in a glass. The extent of the problems with needles depends on the aspect ratio of the needles and the diameter of the capillary used – smaller diameter capillaries usually being more problematic. Figs. 2.10.27 and 2.10.28 show the example of wollastonite powder mounted in 0.3 and 0.2 mm capillaries, respectively, where orientation effects become pronounced in the 0.2 mm capillary. Fortunately, needle-like morphology is observed more often in organic crystallites, where larger-diameter capillaries can be tolerated.

Glass and fused silica ('quartz') capillaries can be bought commercially in a range of diameters between 0.1 and 2 mm. Different compositions of glass are available that have varying absorption characteristics (Table 2.10.3). The softer glass has a greater tendency to splinter but can be heat-sealed very easily by melting. Quartz tends to be stiffer and often breaks more cleanly when scored using a cutting stone, but requires a hydrogen flame for heat-sealing because of its high melting point. Alternative methods of sealing the open end of capillaries include using molten wax, epoxy and nail varnish. The choice may be restricted by the environment in which the capillary is being filled. In an argon-filled glove box the use of a flame or solvent-based method may not be feasible or desirable, whereas wax sealing with a heated filament is acceptable.

The small size and delicate nature of capillaries can make them extremely frustrating to fill, especially in environments such as glove boxes. Patience is an absolute must, especially with valuable or small samples where capillary breakage and sample loss are unacceptable. It is very important to make sure that the sample is fine enough to pass into the capillary without jamming. Even if it is fine enough, different powders can vary considerably in their tendency to aggregate. For example, NIST 640d silicon contains fine crystallites and flows extremely well, making it very easy to load into a capillary. However, some rutile powders can be very fine but don't flow well, making them difficult to load into smaller capillaries.

Once the small amount of material is in the capillary funnel (assuming it is a commercial capillary), it must be coaxed to drop to the bottom. This is usually done using some form of vibration. Anything from dedicated capillary-filling machines to ultrasonic baths, test-tube vibrators and nail files can be used. A common strategy is to drop the capillary down a vertical 50 cm glass tube, and allow the bouncing when the capillary hits the bottom to vibrate the sample. However, with very small and/or valuable samples the risk of the sample being vibrated out of the funnel may be too great to use automated techniques. In this case, very gently stroking the capillary using a fingernail to induce a low-frequency vibration may be the best option, changing the position at which the capillary is held to alter the vibration frequency as required. Agglomerates blocking a capillary can be very difficult to break up by vibrating the capillary manually, but an ultrasonic bath can often break up loosely bound agglomerates. Using a smaller-diameter quartz capillary or wire to tamp down a clog is possible, but riskier than using an ultrasonic bath.

Table 2.10.3
Absorption and physical characteristics of the capillaries whose data are shown in Fig. 2.10.46

Material	Linear absorption, Cu $K\alpha$ (cm^{-1})	Wall thickness (μm)	Outside diameter (mm)
Quartz (Hampton Research)	76	10	0.50
Soda lime glass (Hampton Research)	126	10	0.50
PET (Advanced Polymers)	10	19	0.58
Polyimide (Cole-Palmer)	9	25	0.55

The most commonly used capillaries range between 0.3 and 0.8 mm in diameter. Capillaries with a diameter less than 0.3 mm are extremely difficult to fill and very large ones can cause unwanted artifacts. For moisture-sensitive materials it is worth noting that significant moisture can adhere to the interior surface of commercial glass and quartz capillaries, so heating them in an oven prior to use is recommended.

The interplay between the sample absorption, radiation and optics can make the choice of capillary material and diameter a dynamic one. The capillary absorption is measured using the term μR, where μ is the effective linear absorption coefficient (taking account of the sample density) and R is the capillary radius. A convenient tool for estimating capillary absorption is available on the 11-BM web site (http://11bm.xray.aps.anl.gov). Ideally, the value of μR should be less than 3 for the absorption corrections in most software packages to adequately cope with the effect of absorption. A recent analytical correction has been shown to be effective to $\mu R = 10$ (Lobanov & Alte de Viega, 1998), but is not yet implemented in all current analysis software. A pre-analysis correction is always possible but not ideal. The effect of high capillary absorption can be seen visually by a reduction in peak intensity at lower angles, which correlates with the displacement parameters in a structure refinement. The easiest way to change μR is by changing the capillary diameter. More heavily absorbing samples usually require smaller capillaries, although using an alternative radiation such as Mo $K\alpha$ to change the linear absorption coefficient is a possible alternative. Determining an accurate sample packing density experimentally can be tricky. There can be significant variability between supposedly identical capillaries, so ideally the empty portion of the actual capillary being used should be measured. The packing density generally ranges from 20–50% depending on the morphology of the crystallites and the amount of energy applied in vibrating the sample into the capillary (*e.g.* sonicating the sample will increase the packing density).

references