

2.10. SPECIMEN PREPARATION

Zachariasen (1945) described an extinction correction (model) including terms relating to crystallite size, wavelength, structure factor and scattering angle. Extinction effects will be apparent with large crystallites and long wavelengths. Extinction effects are also greater for the more intense (low-angle) reflections, so extinction mimics the effects of small displacement parameters. In a single-phase system, unexpectedly low or even negative displacement parameters may be the only sign that extinction effects are present. In a multiphase system the effects of extinction will reduce the apparent phase fraction of the affected phase with respect to the rest of the sample. In fact, studying extinction experimentally is often done by using its effects on quantitative phase analysis to untangle the different effects (Cline & Snyder, 1987). The frequently high quality of natural quartz makes the quantitative phase analysis of mineral samples the most likely scenario for the appearance of extinction in a practical laboratory setting.

The wide range of wavelengths and wide range of $(\sin \theta)/\lambda$ used in time-of-flight (TOF) neutron diffraction makes extinction effects particularly pronounced. Consequently TOF data often require the application of an extinction correction (Sabine *et al.*, 1988). Constant-wavelength neutron diffraction frequently uses longer wavelengths than normally used in the laboratory or synchrotron beamlines, so the user must be aware of possible problems.

Despite the danger of ‘message fatigue’, the dependence of primary extinction on crystallite size adds yet another reason to reduce the crystallite sizes to the order of 1 μm or so. Theoretically, single-crystal silicon will exhibit extinction with copper radiation with crystallite sizes of 5 μm .

2.10.1.4. Holders

2.10.1.4.1. Reflection sample holders

In a laboratory setting these are the most common type of holders – normally for use in a Bragg–Brentano instrument. A wide variety of sample holders for different applications are available. Several different holders and techniques will be described, but there are some issues common to all holders in reflection geometry, particularly with Bragg–Brentano geometry.

In Bragg–Brentano parafocusing geometry care should be taken that the surface of the sample is flat. If the surface is not flat the parafocusing condition is violated and will degrade the peak resolution and positions; in addition, surface roughness can affect the intensities. Where there is a cavity it seems straightforward to make sure that the sample surface is level with the top surface of the holder. The peak positions obtained in Bragg–Brentano geometry are very sensitive to specimen displacement; a vertical displacement of 20 μm in a typical diffractometer will shift the peaks by approximately $0.01^\circ 2\theta$. The derivation of the equation for the effect of displacement on peak position is given in Fig. 2.10.31. The minus sign in the equation reflects the convention that the displacement is positive if it increases the radius of the

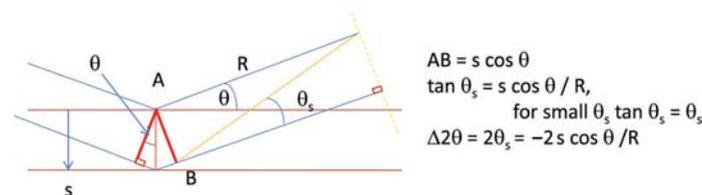


Figure 2.10.31

Derivation of the equation relating peak displacement to sample displacement (s) in parafocusing geometry. R is the goniometer radius.



Figure 2.10.32

A home-made top-loading zero-background silicon holder with a 0.5 mm deep cavity.

diffracting circle, *i.e.* the sample is too low. Front-packed specimens are almost always too high, so the analyst needs to refine his/her technique to minimize the displacement errors.

The sensitivity to specimen displacement is such that even dirt between the reference surface of the sample stage and the holder can produce a detectable peak shift. Dust accumulation inside a powder diffractometer is almost inevitable, so occasionally cleaning these surfaces is recommended.

Parallel-beam-geometry diffractometers have become popular in many laboratories because some of these problems are avoided. Although there are often some disadvantages in terms of peak resolution and grain sampling, they allow more flexibility in the mounting of specimens. For instance, rough sample surfaces and displacements do not cause the aberrations that are apparent in data from conventional parafocusing diffractometers when the same samples are analysed with a parallel-beam system.

Many different types of holders for reflection geometry are available commercially from the instrument vendors, but often home-made holders can be equally effective and customized for specific tasks. Most common are the different types of top-loading sample holders made from plastic or metal, often with a cavity to hold the sample. Commonly the cavities are larger or smaller than those offered by the vendors. The cavity may include some form of zero-background plate such as specially cut single-crystal silicon (Fig. 2.10.32) or quartz, although this does add a significant cost. Some quartz plates may exhibit forbidden reflections or contain inclusions, so they should be tested before use in a sample spinner.

In addition to the standard holders, more specialized holders may be bought or built, or indeed fabricated using a 3D printer. These include holders for air-sensitive samples (Fig. 2.10.33), back-loading (Fig. 2.10.34) and side-loading holders, holders for filter papers, clay samples *etc.* Any laboratory with a competent workshop can construct a wide variety of holders, including those for complex *in situ* work, which is discussed in Chapter 2.9. One common theme is that any material in the X-ray beam path must be kept to a minimum to reduce attenuation. Ideally any such material (such as the polymer dome of the air-sensitive holder shown in Fig. 2.10.33) should be as far away from the diffracting plane as possible. A secondary monochromator can be effective in stopping the parasitic scattering from reaching the detector, but with a PSD there is greater reliance on good design to reduce it as much as possible. A common approach with home-designed and -constructed sample holders for air- or moisture-sensitive samples is to cover the sample with a thin Kapton or Mylar film attached with a bead of silicone grease.

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Figure 2.10.33

Commercial holder for air-sensitive samples. This particular holder for small samples has a flat silicon zero-background plate and a polymer dome which screws down against a rubber o-ring seal.

One of the most common questions asked by users of laboratory instruments is how to deal with small sample sizes. In an ideal world, a specialist microdiffraction system or capillary geometry could be used, but many laboratories do not have access to such equipment. How problematic such samples can be depends to some extent on the mass absorption coefficient of the sample. Conventional powder diffraction data relies on having a sample with an ‘infinite sample depth’. However, that depth can be very small for samples with very high absorption coefficients. In those cases, spreading the sample in a very thin layer can still yield reasonable relative intensities across a large range of 2θ angles. With low-absorbing samples such as organics the relative intensities will drop off at higher angles as the sample is no longer



Figure 2.10.34

Filling a commercial back-loading sample holder. The holder is held against a base surface (sandpaper in this case) while filling, the back is replaced and then the holder is flipped over to reveal the sample surface once the clips are removed.

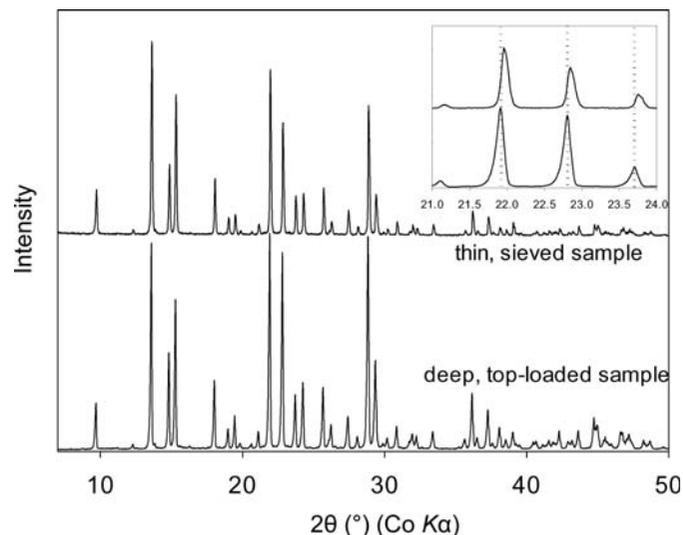


Figure 2.10.35

Data from powdered sucrose on a Bragg–Brentano instrument, with the peak intensities normalized to the first reflection. The thin sample was prepared by sieving onto a low-background silicon plate made slightly tacky using hairspray. The inset shows that there is a slight peak shift between the two data sets as well as the predicted decay in relative intensities with the thin sample with 2θ angle.

‘infinitely thick’, as shown in Fig. 2.10.35. However, the peak positions will be more accurate than with deeper samples because of the lack of transparency effects in thin samples. Consequently, it is not uncommon to obtain two data sets from such samples: from a thin sample to obtain good peak positions, and from a deep one to obtain better relative intensities. The details of sample penetration are given in Chapter 5.4.

Most modern holders are circular and the specimen is often loaded into a round cavity. As the beam ‘footprint’ is rectangular, this is not the most efficient use of the material, as a significant portion will always remain outside the beam. Prior to the introduction of sample spinners, square and rectangular cavities were quite common. It is good practice to know the footprint of the beam at various diffraction angles by observing the illuminated area of a fluorescent specimen. Should the material be in particularly short supply and sample spinning is not absolutely necessary, the powder may be mounted in the minimum rectangular shape to be illuminated by the incident beam. Such an approach may be combined with the use of motorized divergence slits to maintain a constant beam length on the sample. Although most analysis software assumes constant divergence slits, the correction is well known and implemented in most commercial software.

In order to avoid background from the sample holder, thin specimens are usually mounted on flat zero-background plates. It is useful to have the surface of the plate lower than the reference surface ($50\ \mu\text{m}$ is a common value) to minimize specimen displacement effects. In practical terms, thin samples are historically referred to as smear mounts. Slurry mounting using ethanol or acetone often yields a self-adhesive specimen, but it is tricky to obtain the correct slurry rheology to produce a non-lumpy, thin and even layer across the surface; surface roughness is often apparent in the pattern. Loose, friable samples may be problematic with spinning specimens or the tilting specimens in θ – 2θ geometry. A number of materials have been used over the years to adhere thin powder samples to flat plates; common ones are thin smears of Vaseline or grease, but analysts often have their own favourites. The particular material used to stick the sample to the surface is often the result of testing a large number

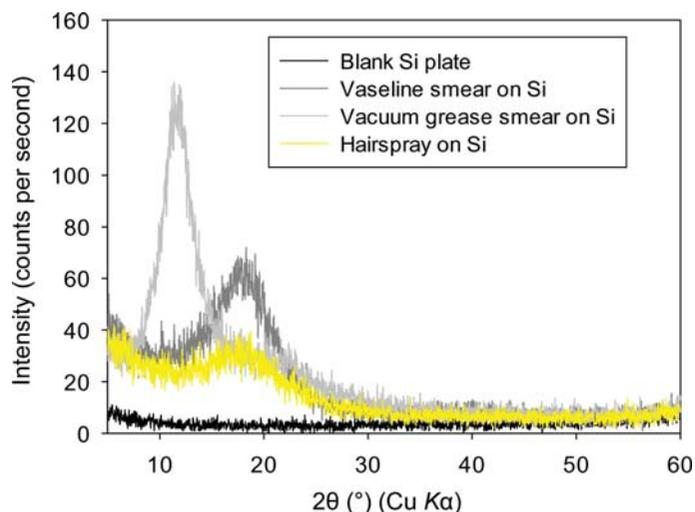


Figure 2.10.36

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

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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.

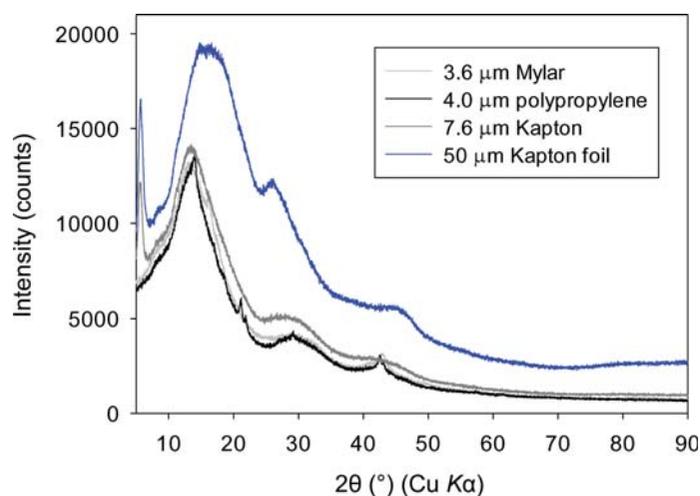


Figure 2.10.38

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

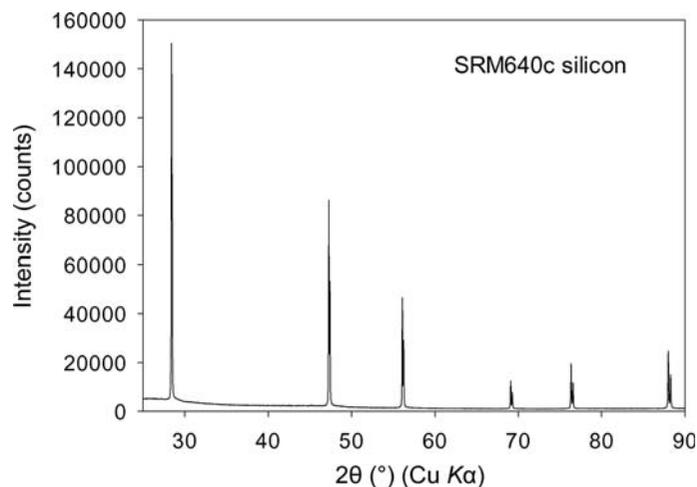


Figure 2.10.39

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

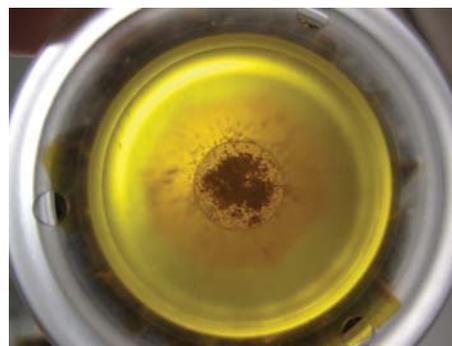


Figure 2.10.40

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

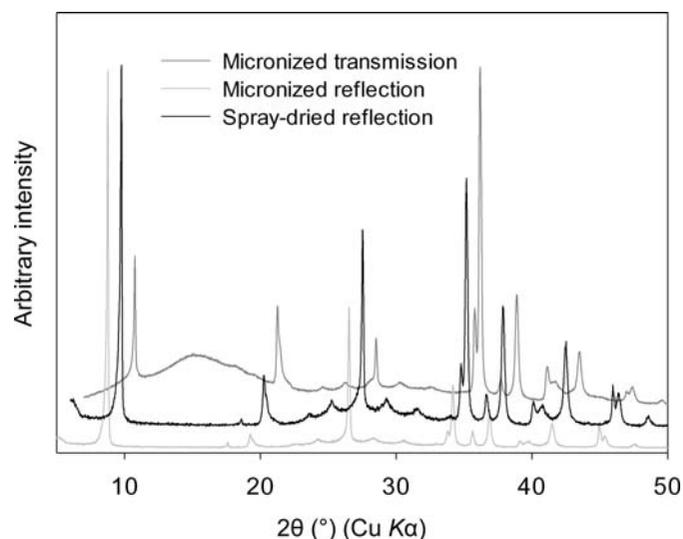


Figure 2.10.41

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 $+1^\circ$ and $+2^\circ$ 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

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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 coaxied to drop to the bottom. This is usually done using some form of vibration. Anything from dedicated capillary-filling machines to

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

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.

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).

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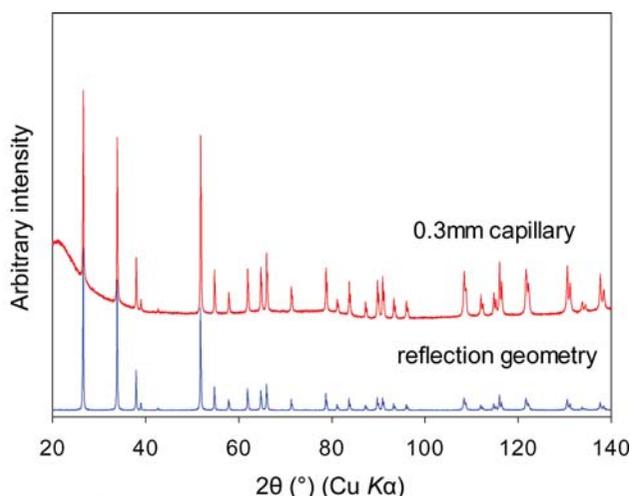


Figure 2.10.42

Comparison of the diffraction patterns of pure SnO_2 from a 0.3 mm quartz capillary in transmission and reflection geometries with $\text{Cu K}\alpha$ radiation. The very high absorption of SnO_2 leads to severe attenuation of the lower-angle reflections in the transmission data.

Where contaminating the sample is acceptable, another option is to dilute the sample with a material with very low absorption to reduce the overall sample absorption. There are two options here: either an amorphous material or a crystalline one. The addition of an amorphous material such as fumed silica (others could include amorphous boron, carbon black *etc.*) does not add any additional reflections to the pattern but will increase the background. Given that the backgrounds of capillaries using $\text{Cu K}\alpha$ radiation are often quite high already, this may not be desirable. Alternatively, a material such as diamond powder can be used, which will add a small number of lines at high angles but does not add to the background. The closely defined crystallite sizes of diamond polishing powder can also improve the flow characteristics of materials that tend to agglomerate. The phase purity of polishing media is not relevant to their intended use, and some diamond polishing powders can contain some SiC , corundum or quartz. Check the phase purity of any diluting phase before use.

Fig. 2.10.42 shows the pattern from a 0.3 mm capillary of pure SnO_2 (cassiterite) taken with $\text{Cu K}\alpha$ radiation compared with that from reflection geometry. The linear absorption coefficient of SnO_2 with $\text{Cu K}\alpha$ radiation is $\sim 1400 \text{ cm}^{-1}$. Assuming a 50%

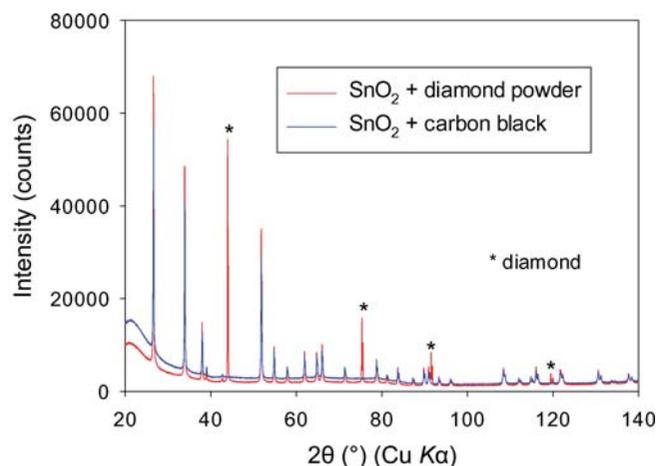


Figure 2.10.43

Raw diffraction data from 0.3 mm capillaries of SnO_2 diluted with 8000 grit diamond powder and carbon black. In each case the capillaries had approximately the same packing density of SnO_2 , so yielded almost identical intensities.

packing density, μR with a 0.3 mm diameter capillary is 10.5, which is much higher than can be tolerated in any structural analysis. Absorption attenuates the lower-angle reflections as the X-rays cannot penetrate properly compared to the high angles. However, in addressing capillary absorption, less really can be more. Fig. 2.10.43 shows data sets from SnO_2 diluted with 8000 grit diamond powder and with amorphous carbon black. As expected, the background is higher with the amorphous carbon but without the additional reflections from the diamond powder. Despite there being only approximately 10 vol% SnO_2 in each of the sample mixtures, the raw low-angle intensities are much higher, and the relative intensities are comparable with those from the reflection data in Fig. 2.10.42. Assuming a 50% packing density for the mixture, the value of μR with a 0.3 mm capillary would be approximately 2.3, which is in the acceptable range for structural analysis.

The relative intensities are such that a good-quality Rietveld refinement of a heavily absorbing compound such as SnO_2 with $\text{Cu K}\alpha$ laboratory data can be easily carried out. Fig. 2.10.44 shows the fit of the diamond-diluted sample to the literature cassiterite SnO_2 structure. With very high dilution factors one should be careful not to compromise the particle statistics too much. Utilizing the full width of the detector with a full capillary will maximize the available statistics.

An alternative approach to dilution of heavily absorbing samples inside a capillary is to coat the outside (or inside) of a capillary. An appropriate absorption correction for annular samples does exist (Bowden & Ryan, 2010), so this is not an impediment. However, it is not available in common software packages so may have to be applied to the raw data prior to a structural analysis. One requirement is that a known thickness of sample needs to be applied to the surface of the capillary as uniformly as possible. This can be difficult to achieve and may require the use of an adhesive to bond the sample sufficiently to the capillary while spinning. The additional effect of an adhesive on the background should be considered in the same way as for a smear mount. Similar results to dilution may be achieved if done with care, as shown in Fig. 2.10.45.

Depending on the instrument geometry, a large diameter capillary can have an additional effect. Where an instrument does not have a focusing geometry (either primary or secondary), the peak resolution is degraded with increasing capillary diameter. With organic samples this can lead the analyst to use a smaller

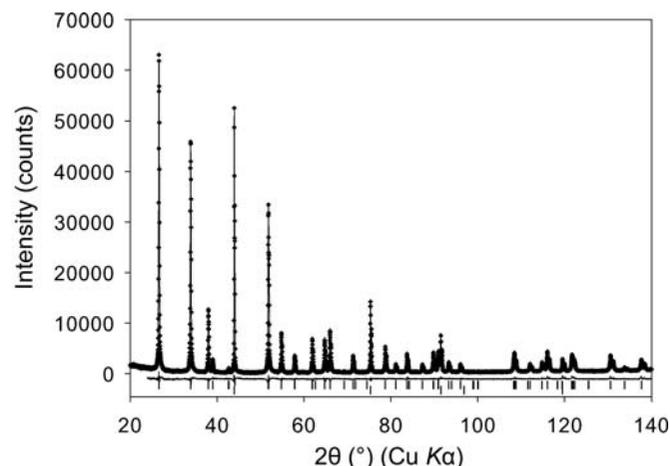


Figure 2.10.44

Rietveld refinement of the diamond-diluted data with the SnO_2 cassiterite structure. The capillary background was subtracted prior to the fitting whilst maintaining the correct counting statistics. The R_w value for this fit was 8.4%.

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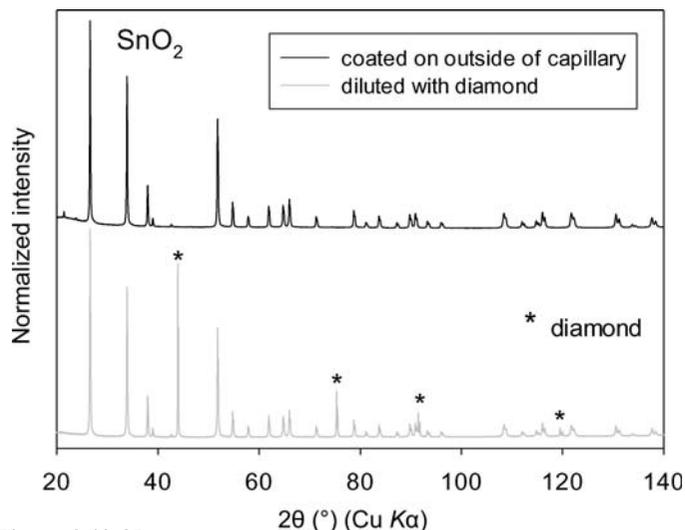


Figure 2.10.45
Comparison of data from SnO₂ when diluted with diamond inside a 0.3 mm capillary and pure SnO₂ coated on the outside of a 0.3 mm capillary.

diameter capillary than optimal to retain reasonable resolution. Consequently, with organic samples where capillaries of 0.8 mm diameter are commonly used, it is highly recommended that an instrument with a primary focusing monochromator (or mirror) is used; the focus should be at the detector. Where the diffractometer is θ - θ geometry it is best to still collect capillary data as if it were a θ - 2θ Debye-Scherrer instrument, simply by collecting 'detector scans' or the equivalent in the data-collection software. This has no effect on the data in a perfect situation, but it means that the sample illumination is constant over all diffracting angles even if there is a misalignment of the primary beam with respect to the capillary axis (caused either by misaligned optics, a misaligned capillary stage, or both). In addition, a correction for capillary displacement can be applied to data collected in conventional Debye-Scherrer geometry (Klug & Alexander, 1954) as the x and y displacements relative to the incident beam are constant over all 2θ angles.

Polymer capillaries are becoming increasingly common and are the standard at many synchrotron beamlines. They are easy to seal, but the lack of a funnel can make smaller sizes

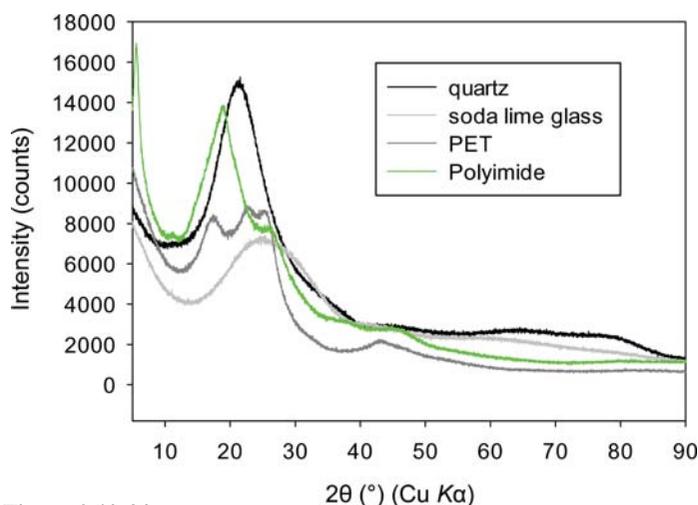


Figure 2.10.46
Comparison of the background from four different 0.5 mm-diameter capillaries. The quartz and glass capillaries are commercial capillaries for diffraction analysis. PET and Kapton capillary tubing are available from a number of different suppliers and are not made specifically for diffraction.



Figure 2.10.47
Platform and pin mounts for capillary samples.



Figure 2.10.48
A 0.5mm capillary secured into a standard brass capillary pin using dental wax at both ends of the pin.

trickier to fill. A number of polymers can be used for capillaries, e.g. Mylar [poly(ethylene terephthalate) – PET] and Kapton [poly(oxydiphenylene pyromellitimide)]. The background from the capillary material itself is often more noticeable with a laboratory diffractometer than for higher-energy synchrotron instruments. A comparison of the background with a Cu K α focusing mirror laboratory diffractometer from 0.5 mm quartz, soda lime glass, PET and polyimide capillaries is shown in Fig. 2.10.46. A study of the different options for polymer capillaries in the laboratory environment was published by Reibenspies & Bhuvanesh (2006), which highlighted the awkward reflection with polyimide visible just above 5° 2θ in Fig. 2.10.46. It is also worth noting that the walls of polymer capillaries are not as stiff as those of quartz capillaries. If a low-temperature or other experiment might produce an internal vacuum (*i.e.* freezing a liquid sample), a polymer capillary can deform from a perfect cylinder, which may cause problems.

Mounting the filled capillary on the goniometer head can be achieved in different ways. Most commonly a hollow brass pin is used, but flat platforms are available (Fig. 2.10.47). The various pins/platforms are a standard size, so they should fit no matter where they are sourced from. The flat platforms have a hole in the middle, but it is only suitable for inserting small-diameter capillaries. Large-diameter capillaries must be affixed to the platform surface with wax and are vulnerable to sagging with horizontal goniometers because of the lack of support. The brass pins will accept larger capillaries and are to be preferred with respect to improved support for the capillary where the capillary is held at both ends of the brass pin (Fig. 2.10.48). Fixing the capillary onto the base is often done using wax or clay, although epoxy may be preferable if elevated temperatures are to be used. Coarse alignment is usually performed using a small desktop microscope before final alignment on the system. It is important to try to get the capillary rotating as straight as possible before mounting on the system, as removing tilt errors is much more difficult with the higher-magnification alignment scope mounted on the goniometer. Final alignment of a capillary is an exercise requiring patience. Never try to align out errors in two directions at once. Even if repeated attempts are necessary to stop the goniometer head in the correct position (Fig. 2.10.49), only correct errors perpendicular to the view in the scope. Ideally, the final alignment should only require correction of a side-to-side

2. INSTRUMENTATION AND SAMPLE PREPARATION

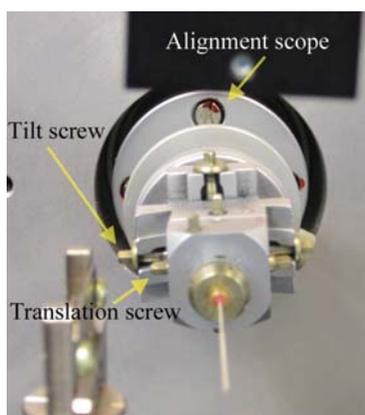


Figure 2.10.49
Goniometer head position in relation to the goniometer-mounted alignment scope.

movement rather than any wobble from tilt misalignment. However, it can still take some time. For systems where the goniometer spinning is controlled by computer software a wireless computer mouse is a very good investment, as it allows the person performing the alignment to stop the spinning capillary without taking their eyes off the sample.

2.10.2. Neutron powder diffraction

2.10.2.1. Specimen form

Large penetration depth and sensitivity to lighter elements (especially mobile species such as hydrogen, lithium and oxygen) in the presence of heavier elements make neutron diffraction a powerful and complementary technique to X-ray diffraction for structural studies. Because neutrons are highly penetrating and large sample volumes can be used, sometimes no specimen preparation is needed at all; sintered ceramic pellets, fish otoliths and renal calculi can be placed directly in the beam. However, the most traditional sample holder for standard neutron powder diffraction (Debye–Scherrer geometry) is cylindrical and is usually made of vanadium. If the diffraction instrument has reflection geometry, however, one has to use flat plates. Diffractometers built for the study of engineering materials can accommodate various shapes and forms because they can isolate small volumes within the sample.

2.10.2.2. Sample size

Traditionally, a large amount of sample was needed for neutron powder diffraction because of the limited flux available at various neutron sources. However, significant advances have been made in source power and detector technology, making it possible to do standard diffraction experiments with relatively small quantities of samples, both at reactor and spallation sources. There are multiple factors that have to be taken into account to determine how much sample is required. These include source power, detector coverage of the instrument, source-to-sample distance, the scattering power of the sample, beam size, available time and information sought from the measurement. Neutron powder diffraction instruments often have to trade intensity for resolution, and so often a larger quantity of sample is needed for high-resolution instruments. Sample mass can vary from milligrammes to several grammes, so it is always advisable to contact the scientists responsible for the particular instrument to determine the quantity needed for the proposed measurements.



(a)



(b)

Figure 2.10.50
Two examples of sample holders used in neutron powder diffraction. (a) A cell made of Inconel used for hydrogen absorption studies in Li_3N (Huq *et al.*, 2007). (b) Vanadium holders that were specially made for a sample changer built for the Powgen diffractometer located at Oak Ridge National Laboratory.

2.10.2.3. Specimen containment

The choice of materials for designing sample holders usually depends on the type of experiments, temperature or pressure conditions, the type of neutron source (constant-wavelength or time-of-flight), the presence or absence of fine radial collimators in the instrument and finally the sample. The scattering of vanadium ($\sigma_{\text{coh}} = 0.0184 \text{ b}$) or a TiZr alloy (a null scatterer, because of exact matching of the negative scattering length of titanium and the positive scattering length of zirconium) is almost purely incoherent, making it ideal for sample containment for diffraction measurements. Although the coherent scattering of vanadium is small, in careful work it should not be a surprise to find weak peaks from V (space group $Im\bar{3}m$, $a = 3.027 \text{ \AA}$) in the powder pattern. Examples of vanadium sample cans are shown in Fig. 2.10.50(b). At a reactor source aluminium is even better if low-angle (large d -spacing) reflections are of interest, as in the case of many magnetic structural studies, because the aluminium incoherent scattering cross section is three orders of magnitude less than that of vanadium. At elevated temperatures, vanadium easily forms oxides or hydrides in the presence of air or hydrogen, making the cell brittle, so its use is limited to low-temperature studies or in vacuum furnaces. At temperatures higher than 1273 K one often has to use boron nitride caps and molybdenum screws for vanadium sample holders to avoid eutectic formation (an example is shown in Fig. 2.10.51b). For