

2.10. SPECIMEN PREPARATION

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).

2. INSTRUMENTATION AND SAMPLE PREPARATION

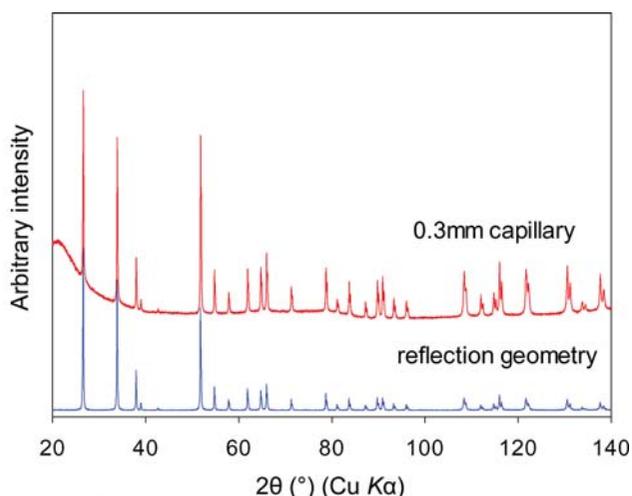


Figure 2.10.42

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%

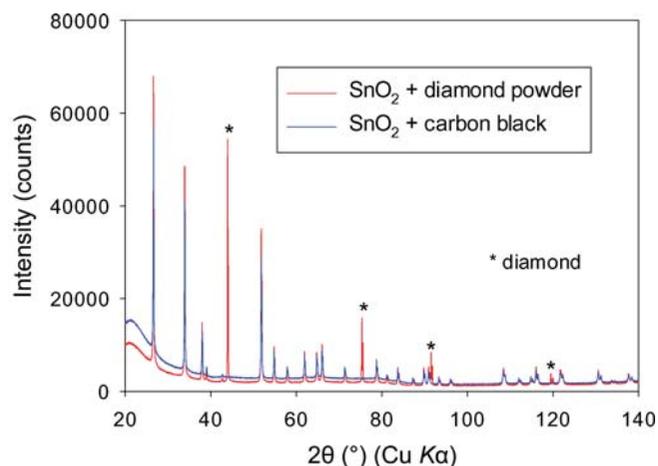


Figure 2.10.43

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

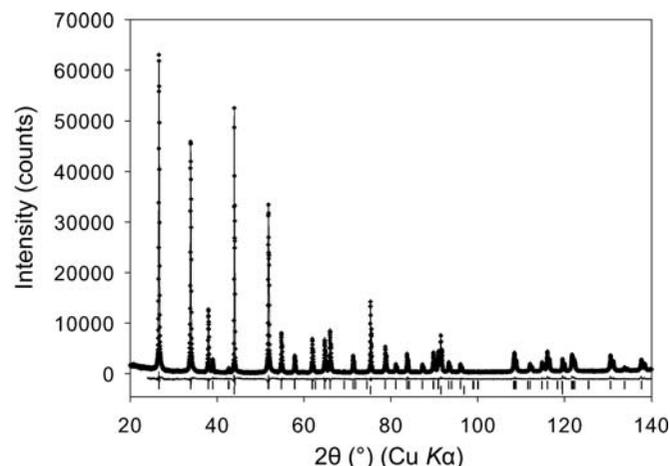


Figure 2.10.44

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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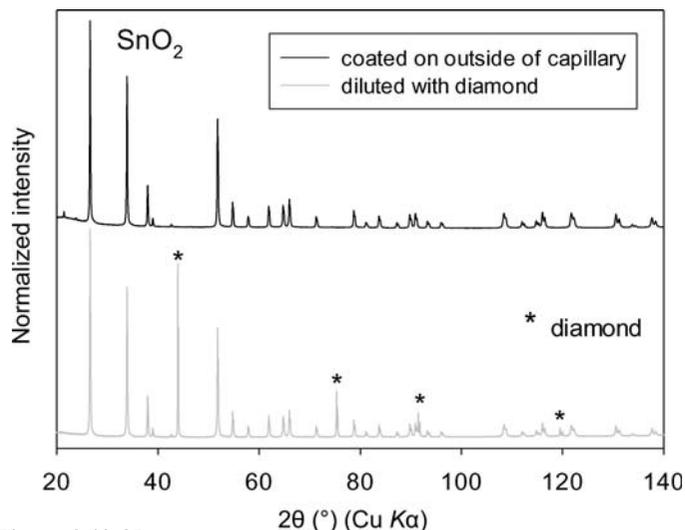


Figure 2.10.45

Comparison of data from SnO_2 when diluted with diamond inside a 0.3 mm capillary and pure SnO_2 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

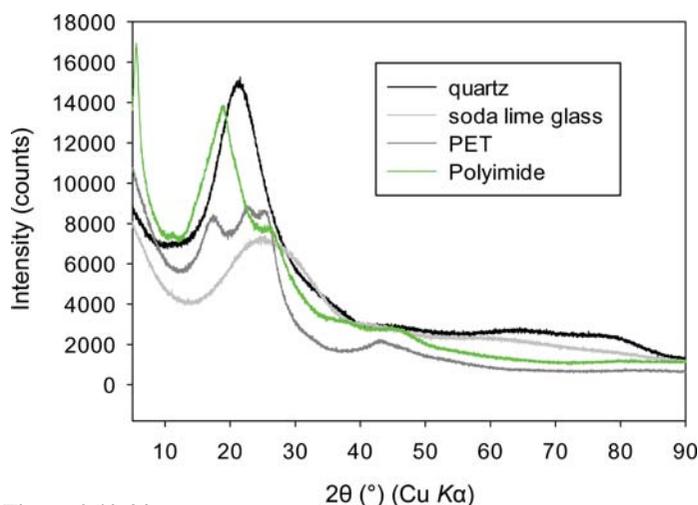


Figure 2.10.46

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 0.5 mm 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 $\text{Cu K}\alpha$ 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 $5^\circ 2\theta$ 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

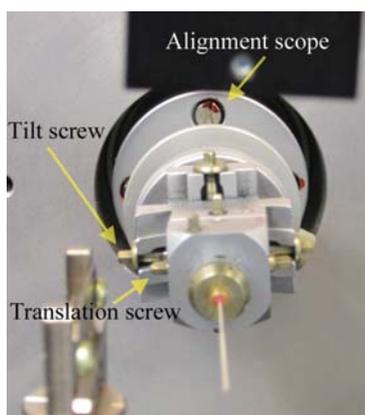


Figure 2.10.49
Goniometer head position in relation to the goniometer-mounted alignment scope.

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