Powder X-ray Diffraction Basic Course Third Installment: Sample preparation and measurement conditions to obtain high-quality data

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1.   Introduction

In the second installment of the powder X-ray diffraction (PXRD) basic course, how to select instrument configurations to obtain high-quality data was described[1]. This third installment provides information on how to prepare samples and determine the best measurement conditions to obtain high-quality data. Regarding sample preparations, the type of sample holders, the effect of grain size of the sample, and the impact of the eccentricity and asperity of the sample surface must be taken into consideration.

In most PXRD measurements, a glass sample holder is usually filled with sample. However, other appropriate sample holders should sometimes be selected based on the chemical properties, composition, and shape of the sample, which will allow you to obtain high-quality data with high resolution and low background. Also, the impact of preferred orientation can sometimes be suppressed. Appropriate optics should also be used for the selected sample holder. The following chapters and sections will describe the details of sample preparation and measurement conditions, along with a few tricks and traps.

2.   Sample Preparations
2.1.   Selecting a sample holder

0.5-mm depth glass sample holders (Fig. 1 (a)) are commonly used for the PXRD measurements. If this is not an appropriate sample holder for your sample, the quality of the measurement data will not be high enough to obtain good results. For example, diffraction peaks from the sample holder may be observed, or a PXRD profile with peak intensity ratios different from theoretical ones may be obtained, and so forth. As a result, erroneous results of qualitative or quantitative analysis might be obtained. To obtain correct results, it is necessary to select a proper sample holder based on the composition, shape, and chemical properties of the sample to be measured. The following subsections describe which type of a sample holder should be used for which type of sample to be measured.

(a) For samples with small linear absorption coefficients

When you measure a sample consisting of light atoms, such as carbon powder or organic materials—in other words, a sample with a small linear absorption

coefficient—the degree of X-ray penetration should be considered. The effective thickness, defined as the thickness of a sample that attenuates irradiated X-rays to 1% of the incident beam intensity, depends on the linear absorption coefficient of the sample. For bulk iron, for example, the effective thickness is 0.019 mm, whereas for bulk carbon it is 4.54 mm for CuKα radiation.

If the optical path length through the sample is longer than the effective thickness, X-rays may be scattered from the sample holder. Also, the packing density of a powder sample is usually lower than that of the bulk sample; which means that X-rays more easily penetrate powder samples and stronger X-rays scattered from the sample holder will be observed. If a sample with a small linear absorption coefficient is filled into a glass sample holder and measured, a broad peak (halo) from the glass sample holder is detected in the 2θ range of 20–30°. If the peak (halo) from the sample holder needs to be avoided, a Si zero-background sample holder
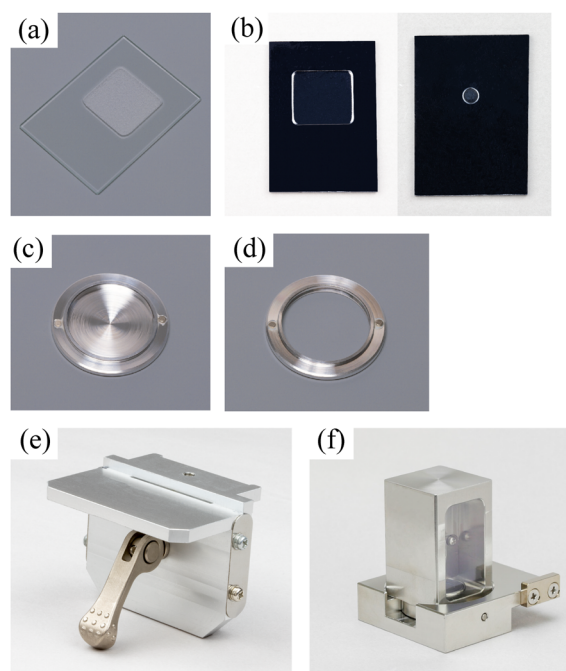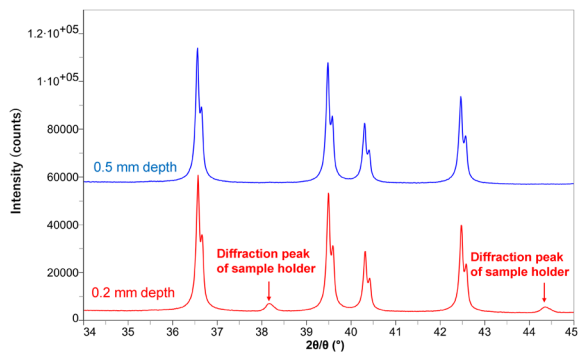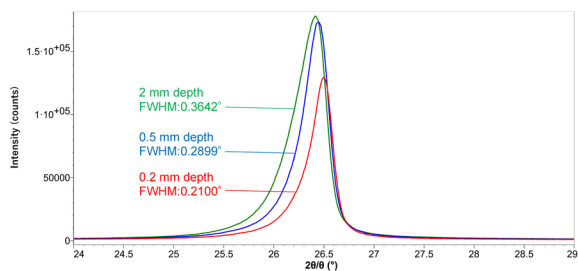

Fig. 1.   Sample holders for PXRD measurements.

(a) glass sample holder, (b) Si zero-background sample holder, (c) Al sample holder for ASC, (d) ring-shaped sample holder for ASC, (e) block sample holder, (f) air-tight sample holder

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Fig. 2. Diffraction peaks from the Al sample holder for ASC. (Wavelength: CuKα, Sample: quartz powder)

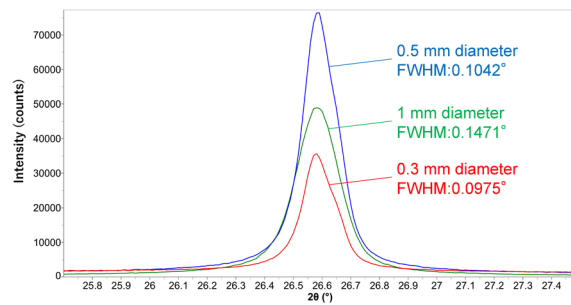**Fig. 3.** Profiles of samples with a small linear absorption coefficient measured using various depth sample holders.

(Wavelength: CuKα, Sample: carbon powder)

Fig. 4. Peak profiles measured using capillaries with different diameters.

(Wavelength: CuKα, Sample: quartz powder)

Fig. 5. Comparison of the PXRD profiles measured using a capillary and films.

(Wavelength: CuKα, Sample: quartz powder)

(Fig. 1(b)) is recommended for PXRD measurements. If an automatic sample changer (ASC) is installed, an Al sample holder for ASC (Fig. 1(c)) is another option. However, please note that, as shown in Fig. 2, diffraction peaks from the Al sample holder may be observed at $2\theta=38.2°$ and $44.3°$ (especially in the case of 0.2 mm depth).
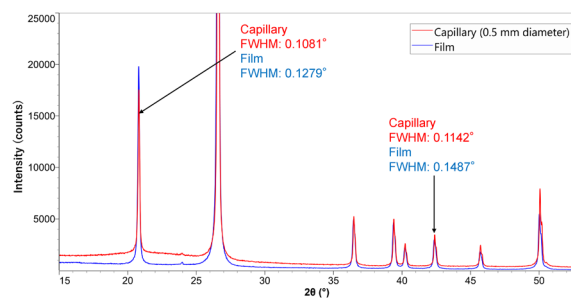
When a sample with a small linear absorption coefficient is measured, X-rays are diffracted from deep in the sample, which causes peak shift and broadening. Therefore, shallow (0.2-mm depth) sample holders are preferrable for samples consisting of light atoms. Figure 3 shows the profiles of carbon powder measured using various depth sample holders. The diffraction peak measured using a 0.2-mm depth sample holder is narrower and more symmetrical than those using the deeper holders.

(b) For highly oriented or coarse-grained samples

Peak intensity ratios in a PXRD profile using an ideal powder sample should be almost the same as the theoretical ratios. If the sample is highly oriented or contains large particles, the peak ratios will be biased. Users need to avoid this bias as much as possible to obtain more precise/accurate analysis results such as qualitative analysis, quantitative analysis, etc. In this situation, the transmission method using a capillary or films is a good option. Compared with the use of a glass sample holder, the impact of pressure during sample preparation is relatively low and preferred orientation can also be suppressed. The impact of preferred

orientation and coarse grains is further suppressed by spinning the sample.

With the transmission method, high-intensity peaks will not be obtained if the irradiated volume is small or if the transmittance of X-rays is small. To obtain high-intensity PXRD patterns, a certain amount of a sample should be filled into a capillary or sandwiched between films so that the transmittance will be $1/e$[*1]. To improve angular resolution when using a capillary, a thinner one (e.g. 0.3–0.5 mm) should be used, although care should be taken to make sure the capillary is well aligned so it does not process or vibrate during data collection. Figure 4 shows peak profiles measured using capillaries with different diameters. The angular resolution declined as the diameter increased. On the other hand, the diffraction peak intensity was highest when using a 0.5-mm diameter capillary. The transmittance ratios using the capillaries with diameters of 0.3 mm, 0.5 mm, and 1.0 mm are 49%, 35%, and 8%, respectively. The transmittance ratio when using a 0.5-mm diameter capillary is closer to $1/e$[*1], and thus the highest intensity was obtained.

For measurements using films, you need to reduce the amount of powder and prepare a thin sample. Figure 5 shows the comparison between the profiles measured using a capillary (red) and films (blue). Using films, the angular resolution became worse and peak intensity became lower in the high-angle region because of the long optical path length through the sample. Therefore, the transmission

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[*1] (e: natural logarithm)

(a)

Si zero−background holder　　Glass sample holder

(b)
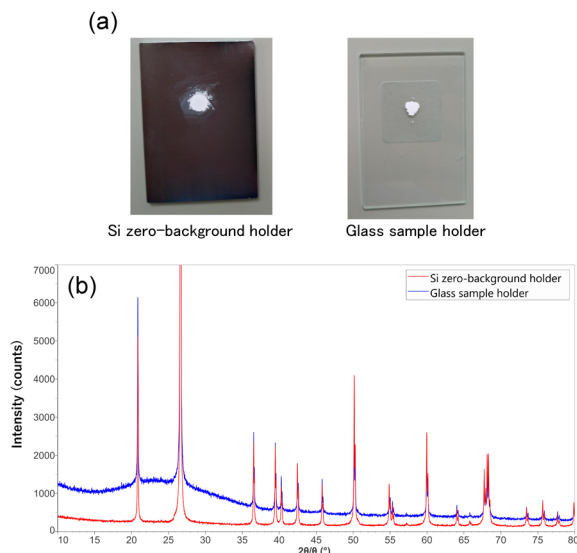
Fig. 6. (a) A small amount (3 mg) of powder samples placed on the sample holders and (b) measured profiles from the samples.
(Wavelength: CuKα, Sample: quartz powder)

Fig. 7. Flowchart for sample holder selection.

method using films is not suitable for measurements on the high-angular 2θ region (more than 40°).

To suppress preferred orientation of a sample in the reflection method, a ring-shaped sample holder for ASC (Fig. 1 (d)) is often used if an ASC-6/8/10 attachment is available. Powder samples are filled into the ring-shaped sample holder from the back side (called the back-loading technique) without smoothing the surface of the sample. Thus, preferred orientation can be suppressed. In addition, if powder samples are filled using a press machine; human error and the eccentric error can be suppressed, which means the back-loading technique using a press machine makes sample preparation highly reproducible.

(c) For a small amount of a powder sample

A Si zero-background sample holder (Fig. 1 (b) and Fig. 6 (a)) is generally used to reduce the background intensity of a PXRD profile; in other words, to increase peak/background ratios (P/B ratios). This means that it is relatively easier to observe small peaks using this holder. For a small amount of powder sample, the Si zero-background sample holder is also useful. A 5-mm diameter indent on the back side of the holder can be used to hold a small amount of powder for reflection measurements. Profiles with high P/B ratios can be obtained because the background intensity derived from the holder is small.

If Si zero-background sample holders are not available, put a small amount of powder onto the center of the back side of a glass sample holder as shown in Fig. 6(a). In this case, the incident slit and the length-limiting slit should be narrowed to reduce background intensity. However, as shown in Fig. 6(b), a broad peak (halo) derived from the glass sample holder is still observed in the 2θ range of 20–30°.

(d) For block-shaped samples
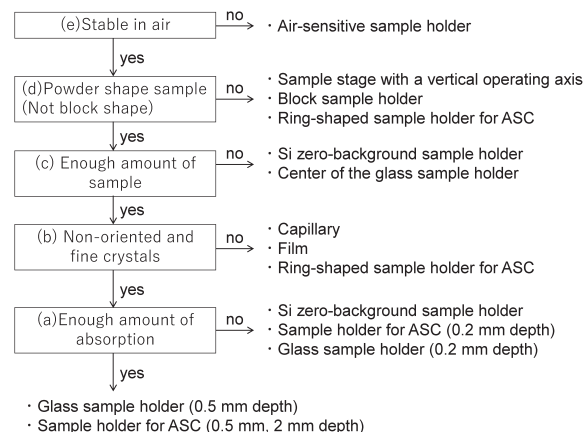
When a block-shaped sample is to be measured, sample height alignment is needed prior to reflection measurements. If a height alignment axis (Z axis) is not installed on the instrument, the sample should be placed on a block sample holder with a Z axis (Fig. 1(e)) using clay or double-sided tape, and the sample height should be aligned using the Z axis. Also, the incident slit should be set to an appropriate width, narrow enough to prevent X-rays from being scattered from the clay or double-sided tape. If the sample surface is not flat, it should be noted that the angular resolution will become worse if using Bragg-Brentano optics, and the positions of diffraction peaks will be shifted due to the eccentricity error caused by the sample.

(e) For air-sensitive samples

If the sample is sensitive to humidity, oxygen, etc., it must be kept from air during measurement. This kind of sample should be filled and enclosed in an air-tight sample holder (Fig. 1 (f)) in a glove box under inert gas atmosphere. Then, the sample can be measured without chemical reactions. There are two types of air-tight holders: with and without a knife edge. With the knife edge, the background intensity in the low-angle region can be reduced; however, the intensities of diffraction peaks at 2θ angles over 60° decrease. Please select the type of air-tight holder depending on the measurement range. Figure 7 shows a flowchart for holder selection. Please select the appropriate sample holder using this figure as a reference.

2.2. Effect of grain sizes

In the PXRD method, it is preferable to measure uniformly sized crystalline particles. Normally, samples should be ground into about 10-μm particles using a mortar or a ball mill. If you sandwich such a fine powder between your fingers (after ensuring that it is safe to touch the sample) and it doesn't have a sandy feeling, the particle sizes are considered to be proper for PXRD measurements. On the other hand, if a powder sample is ground down to much smaller particles (3 μm or smaller in diameter), the peaks will be broadened and peak top intensities will decrease due to the small crystallite sizes (size effect). Furthermore, the amount of amorphous on a particle surface
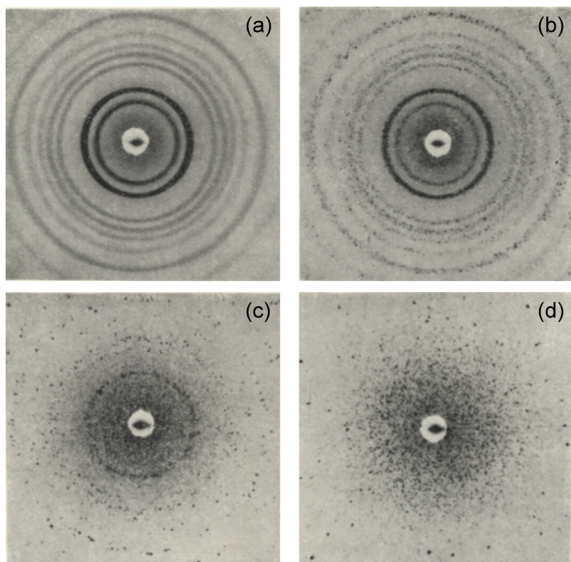
Fig. 8. 2D profiles of quartz powder differing in particle size[2].

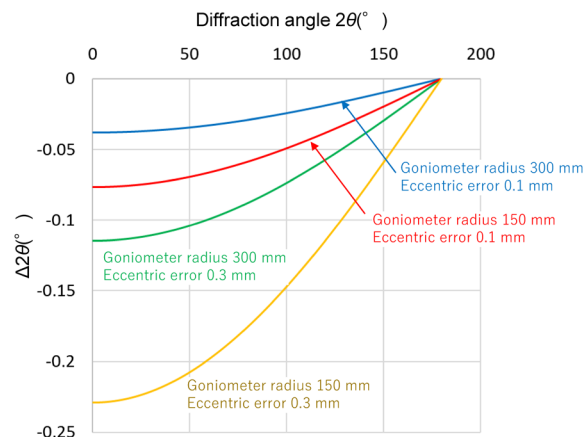Particle size (a) $<10\,\mu m$, (b) $30\,\mu m$, (c) $60\,\mu m$, (d) $90\,\mu m$
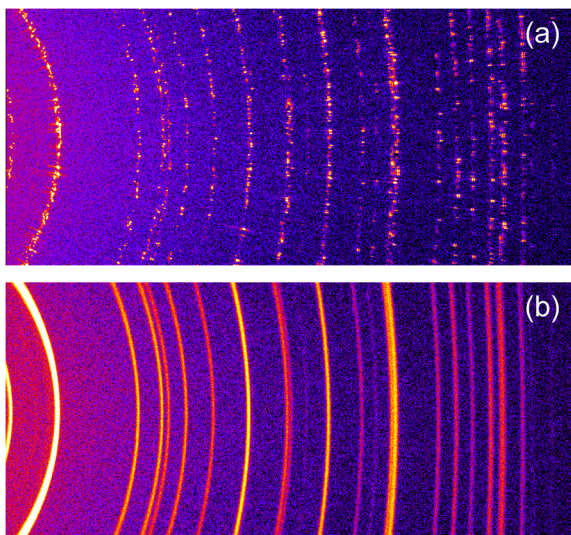
Fig. 9. 2D profiles (a)without and (b)with using a sample spinner.

(Wavelength: $CuK\alpha$, Sample: SiO_2 powder)

Fig. 10. The relationship between the shift amount of peak positions and diffraction angles.

increases (grinding effect); as a result, the crystallite size will become smaller than the apparent size of particles[3].

Figure 8 shows the Debye rings obtained from quartz (α-SiO_2) powder samples with different particle sizes[2]. The larger the particle sizes are, the smaller the number of crystals, and the Debye rings become dotted. (Fig. 8 (b)) If the particles sizes are much larger, distinct rings disappear and PXRD patterns become spotty. (Fig. 8 (c), (d)) PXRD profiles are created by cutting out a section of the Debye rings, which means that the diffraction peak intensity ratios may differ if the particle sizes are large, depending on which cut-out section of the Debye rings is used. This also indicates that refilling reproducibility will be low.

A sample spinner should be used when samples cannot be ground for some reason. Figure 9 shows the 2D images obtained with and without using a sample spinner. Uniform arcs (parts of Debye rings) were observed when a sample spinner was used, which means that the effect of large particles was reduced.

## 2.3. Samples with rugged surface and eccentricity

Especially for a measurement in Bragg–Brentano geometry, the sample surface needs to be as flat as possible, and the sample should be mounted on a sample stage so the sample surface will be placed on the rotation center of the goniometer. In general diffractometers, a sample holder can be mounted at the correct position just by inserting the holder to the sample stage. It is important to fill powders in the indent of a sample holder so that the height of the sample surface matches the reference plane of the sample holder. Peak positions shift to the lower-angle side if the height of the sample surface is lower than that of the reference plane, while they shift to the higher-angle side if the height of the sample surface is higher. In addition, the amount of peak shift is larger in the lower 2θ angle region. Figure 10 shows the relationship between the magnitude of the shift in peak positions and the diffraction angle. Also, the shift amount is larger when the goniometer radius is smaller. Eccentric errors can be reduced by adjusting the sample height using a vertical operating axis (Z axis).

3. Measurement Conditions

The following sections will describe the procedures of how to determine appropriate measurement conditions. Generally, the measurement range and step size are determined first, then the speed is determined.

3.1. Measurement range

It is necessary to include all diffraction peaks from the low 2θ angles to obtain the correct result for qualitative and quantitative analysis. When the sample information is unknown, the PXRD profile should be checked by a preliminary measurement in advance. As an example of preliminary measurement conditions using a one-dimensional (1D) detector: the speed is 50°/min and the
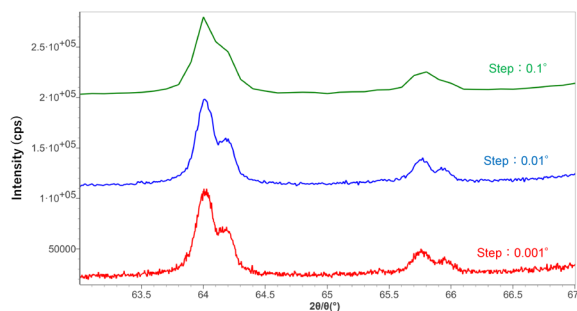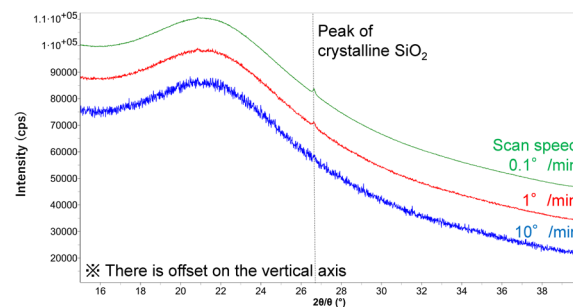
Fig. 11. Profiles measured by different step sizes at the same speed.
(Wavelength: CuKα, Sample: SiO$_2$ powder)

Fig. 12. Detecting a small peak by changing the speed.
(Wavelength: CuKα, Sample: Mixture of crystalline Si of 0.1% and amorphous Si of 99.9%)

2θ range is 3–80°. The data collect range must include the diffraction peak at the lowest angle observed in the quick measurement result. If the starting angle of the measurement is low, the incident slit width should be narrowed; otherwise the incident X-rays will irradiate outside the sample. Since diffraction peak intensity decreases due to the narrow incident slit; the starting 2θ angle should be just a little less than the lowest-angle diffraction peak.

Many diffraction peaks are necessary for a reliable qualitative analysis. Therefore, it is better to measure into the high-angle region. Generally, the upper limits for organic and inorganic materials are $2\theta=60°$ and $2\theta=90°$, respectively.

3.2. Step size

The larger the X-ray intensity measured by a normal photon-counting detector, the smaller the statistical error. The measurement step size is proportional to the X-ray intensity since the counting time at a measurement point is proportional to the step size if the speed is the same. With a larger step size, higher quality data can be obtained in terms of statistical errors arising from X-ray intensities. Figure 11 shows the profiles measured by different step sizes at the same speed. As shown in the figure, the statistical fluctuation of the red profile, where the step size is 0.001°, varies greatly compared to the other profiles where the step sizes are larger. On the other hand, if the step size is larger than the optimal size, it is difficult to reproduce the peak shape, meaning that the correct peak intensity and position cannot be calculated. From these two points of view, the appropriate step size should be determined as 1/7–1/10 of the full width at half maximum (FWHM) of the sharpest peak in the

preliminary measurement profile.

3.3. Measurement speed

Generally, the measurement speed is also determined based on the preliminary measurement profile so that the maximum peak height will be at least 3,000 counts or higher for qualitative analysis and 10,000–20,000 counts for quantitative analysis. Figure 12 shows PXRD profiles with different scan speeds. A small diffraction peak was supposed to be observed at $2\theta=26.6°$, but it is difficult to observe it in the quick measurement profile (blue, 10°/min). Since a slow speed reduces the statistical fluctuation of the PXRD profile, slowing down the speed is sometimes an effective way to detect small diffraction peaks.

4. Conclusion

As described above, proper sample preparation and setting appropriate measurement conditions are very important to obtain high-quality PXRD data. It is particularly worth noting that measurement results can be improved without installing extra attachments or optical systems. It is strongly recommended to optimize your sample preparation and measurement conditions as soon as possible. In the fourth installment, the principles, know-how, and points of qualitative analysis will be described with several examples.

References

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(3) R. L. Gordon and G. W. Harris: *Nature*, **175** (1955), 1135.