# Use of multi-dimensional measurement in powder X-ray diffraction

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## 1. Introduction

In powder X-ray diffraction (XRD) measurements, the measurement mode (0D, 1D, 2D) and optical system are selected to suit the state of the sample and the purpose of the experiment. Until about 10 years ago, the typical approach was a 0D measurement using a scintillation counter (SC) combined with the Bragg-Brentano focusing method (BB optical system) or the parallel beam method. However, due to the development of semiconductor detectors, it became possible to also select 1D and 2D measurement, and the number of optical systems that can be used in combination is increasing every year[1]. This paper presents examples where it is effective to change the measurement mode (0D, 1D, 2D) or optical system when the sample contains trace components, or when particle size or orientation have an effect on the sample. Table 1 summarizes the sample conditions and system configurations explained in this paper. The latest SmartLab SE powder X-ray diffractometer was used for most measurements.

## 2. Detection of trace components

The diffraction peak angle, intensity (or intensity ratio), and peak width are used in powder X-ray analysis. If it is assumed that the measurement of the diffraction peak angle and intensity is uncertain, then the results of crystal phase identification and the quantitative values for crystal phases will also become uncertain. Detection of trace components is an example where measurement of the diffraction peak angle and intensity becomes difficult. Trace components manifest as micropeaks (signals) and are observed on the baseline but, in general, peak detection is difficult if the signal height to noise level (S/N) ratio is not three or higher.

**Table 1.** Sample conditions and equipment configurations treated in this paper.

| Sample | Measured dimensions | Optical system |
|---|---|---|
| Contains trace components | 0D | Focusing method optical system (BB) |
| | 1D | Focusing method optical system (BB) |
| | 1D | Divergent beam optical system obtained from a multilayer mirror (DB) |
| Has effects due to particles or orientation | 1D | Focusing method optical system (BB) |
| | 2D | Parallel beam optical system (PB) -2D slit |

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In other words, suppression of the baseline noise level (vertical amplitude relative to the background base) is crucial for detecting trace components. Thus this paper presents cases of high-speed 1D measurements with a BB optical system and high-speed 1D measurements with a divergent beam optical system (DB optical system) obtained by a flat multilayer mirror.

### 2.1. Effectiveness of high-speed 1D measurement for statistical fluctuation

Figure 1 shows the profile of $\alpha$-quartz when a 0D measurement was performed with an SC. When a single sample was measured using the same system configuration at high speed (20°/min) and low speed (2°/min), the noise level of the profile was smaller for low-speed measurement than for high-speed measurement. This noise is a statistical fluctuation produced in accordance with the X-ray count. If the background can be ignored, then, for example, the standard deviation for a count value of 100 counts is $\sqrt{100}$ counts, i.e., 10 counts, and the relative standard deviation attains a value as high as 10%. That is, the more the count is increased per measurement point, the more the standard deviation is suppressed, and the smoother the data that is obtained. In other words, using a high-speed 1D detector is effective for obtaining high-intensity data in a short time.

Figure 2 shows the profiles for $TiO_2$ obtained through a 0D measurement using an SC, and a high-speed 1D measurement. This sample contains $TiO_2$ as the anatase phase, together with a crystal polymorph rutile phase (0.15 mass%). The micropeak of the rutile phase, which was difficult to detect with the SC, was detected using the high-speed 1D detector.

An XRD profile is composed of the diffraction angle ($2\theta$) detected by diffraction X-rays, and the associated intensity. An SC has no position information on its detection surface, and thus in 0D measurement, the angle of the receiving arm where the detector is placed becomes the diffraction angle on the profile. The angular resolution is produced by a receiving slit or parallel slit analyzer. The width of the receiving slit (RS) set in the BB optical system is, for example, 0.3 mm (Fig. 3), and only X-rays that have passed through this slight gap are counted. The reader can surely imagine how this measurement takes time.

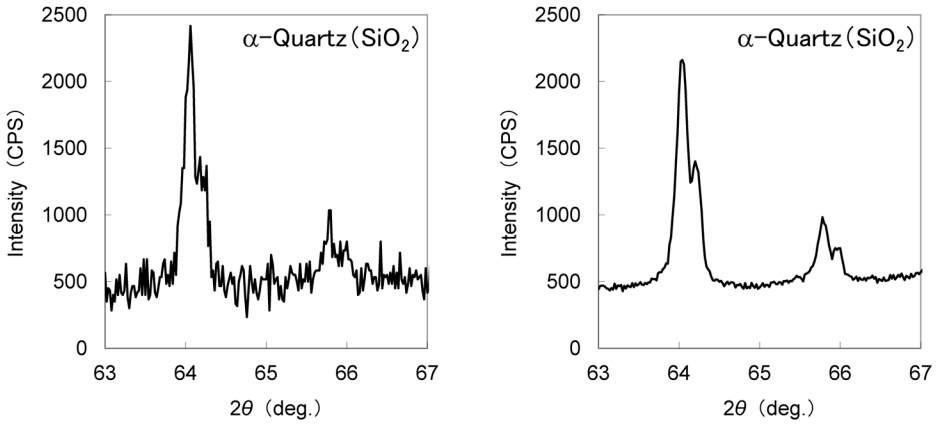


**Fig. 1.** Profile of $\alpha$-quartz measured at scanning speeds of 20°/min (left) and 2°/min (right).

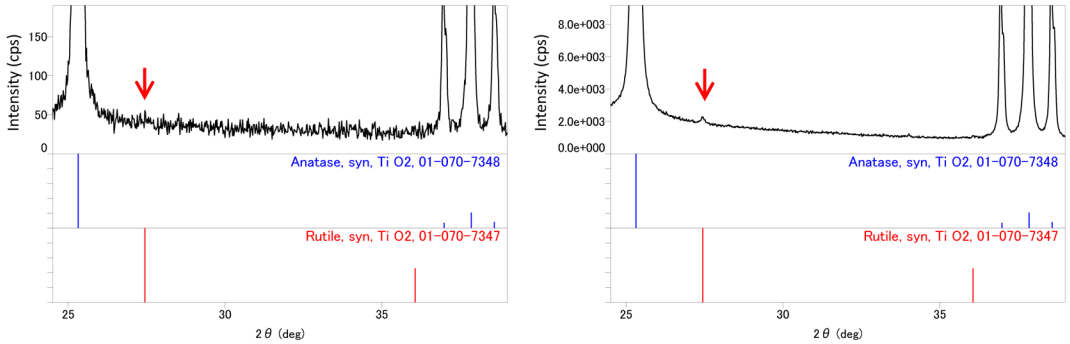


**Fig. 2.** Profile of $TiO_2$ obtained through 0D measurement (left) and 1D measurement (right).
(X-ray output: 40 kV-50 mA, scanning speed: 1°/min)

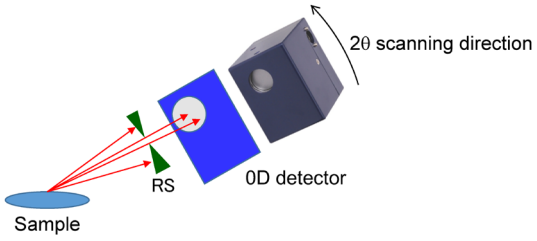


**Fig. 3.** Measurement using a 0D detector.

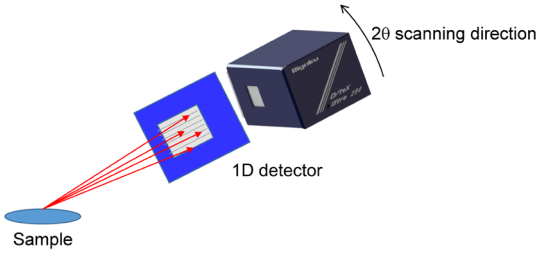


**Fig. 4.** Measurement using a 1D detector.

A high-speed 1D detector, on the other hand, has a layout with multiple long and thin semiconductor detector elements. In the case of Rigaku's D/teX Ultra250, the detection surface is composed of 256 elements with dimensions 20 mm × 0.075 mm. There is position information in the $2\theta$ direction of the detection surface (Fig. 4), and, in 1D measurement, the intensities of X-rays counted by each element are integrated and output. Integrated intensity is output as "intensity" at a specific diffraction angle, and thus intensities 100 times or more greater than 0D measurement are obtained.

## 2.2. Effectiveness of DB optical system for detection of trace components

There are cases where micropeaks cannot be detected simply by using a high-speed 1D detector and increasing the count. X-rays with uniform wavelength, called characteristic X-rays, are used in XRD measurement. However, in the incident X-rays of the BB optical system, characteristic X-rays are mixed with X-rays that have a continuous distribution of various wavelengths (called continuous X-rays). When these continuous X-rays are absorbed by the sample and fluorescent X-rays are emitted, the baseline of the profile increases, and the noise level also increases. In the DB optical system, a flat multilayer mirror is placed between the X-ray generator and sample (Fig. 5). Continuous X-rays contained in the incident X-rays are eliminated by this mirror, resulting in monochromatization to characteristic X-rays only, and thus generation of fluorescent X-rays is suppressed. As a result, the baseline becomes lower, and the noise level also becomes smaller.

Figure 6 shows a comparison of the profiles for a mixture of Cu and $Cu_2O$, measured using a BB optical system and a DB optical system, with a standard

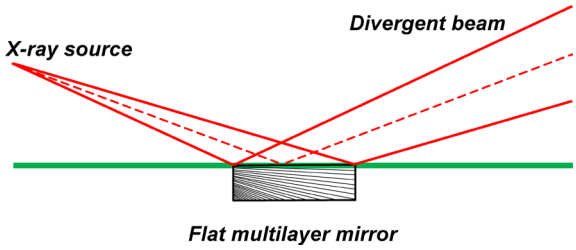


**Fig. 5.** Divergent beam obtained from flat multilayer mirror.

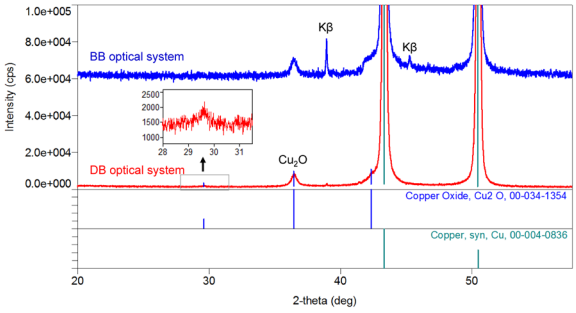


**Fig. 6.** Profiles of mixture of Cu and $Cu_2O$ measured with BB optical system and DB optical system.

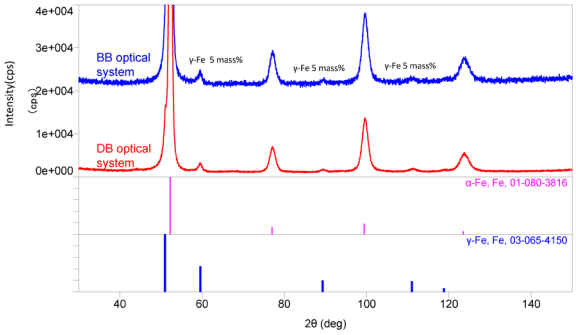


**Fig. 7.** Profiles of mixture of $\alpha$'-Fe phase and $\gamma$-Fe phase measured with BB optical system and DB optical system.

diffraction pattern. If the element Cu is contained in the sample, the produced fluorescent X-rays are CuK$\alpha$ rays, and thus it is impossible to remove them, even with a receiving monochromator. Therefore, with the BB optical system, the background rises, and the noise level of the baseline also increases. As a result, the micropeak for $Cu_2O$ is buried in noise. With the DB optical system, on the other hand, the noise level of the baseline is suppressed, and the shape of the micropeak can be observed.

Figure 7 shows a comparison of standard patterns with the profiles for a mixture of $\alpha'$-Fe (martensite) phase and $\gamma$-Fe (austenite) phase measured with the BB optical system and the DB optical system. In residual austenite quantification, there are cases where CoK$\alpha$-rays are selected as characteristic X-rays, taking into account the improvement in baseline noise, ensuring the number of peaks used for analysis, and the penetration depth of X-rays. With the DB optical system, the rise in the baseline and the peak noise level were suppressed,

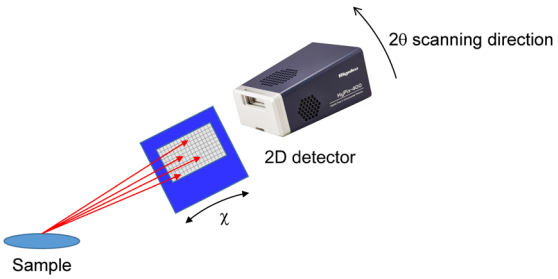


**Fig. 8.** Measurement using 2D detector.

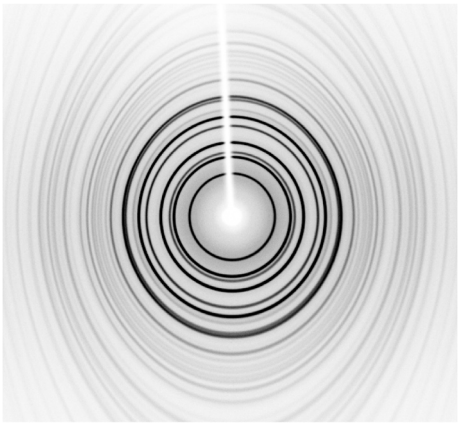

**Fig. 9.** 2D diffraction image for $\alpha$-$Al_2O_3$ (measurement using R-AXIS RAPID II).

and it was possible to detect the peak of the austenite phase (5 mass%) more clearly than with the BB optical system.

## 3. Effects of crystal state on profile

In powder XRD measurement, it is assumed that the crystallites contained in the sample are fine, and that the orientation of crystallites is non-uniform (random). However, measurement must also be carried out with samples that cannot actually be powdered, and with samples in which crystallite directions are aligned (in a preferred orientation) due to cleavability or processing conditions. In 0D measurement or 1D measurement of such samples, there are cases where it is difficult even to identify the crystal phase. In these cases, 2D measurement becomes effective.

Multiple square semiconductor detection elements are arranged in the detectors used in 2D measurement. In the Rigaku HyPix-400, the detector surface is composed of approx. 37,000 elements with dimensions 0.1 mm × 0.1 mm. At the detection surface, there is position information for $2\theta$, and for the x direction orthogonal to it ($\beta$ direction in terms of data) (Fig. 8), and it is possible to detect the diffracted X-rays as a 2D diffraction image.

If the crystallites are fine and the direction of the crystallites is non-uniform (random), then the 2D diffraction image forms a ring shape with no gradations (Fig. 9). However, when the particles become coarse, the 2D diffraction image becomes spotty. Also, even if the crystallites are fine, orientation of the crystallites will cause the 2D diffraction image to take on an

arc-shape. A major feature of 2D measurement is that it is possible to visually determine the condition of the crystallites. There are cases where a special-purpose focusing element or collimator is used to obtain an X-ray beam with a point shape necessary for 2D measurement. By using a 2D slit with SmartLab SE, it becomes possible to carry out 2D measurement more easily. Here, we would like to show the effectiveness of 2D measurements for samples in the form of coarse particles, and samples with preferred orientation.

### 3.1. 2D measurement of samples in the form of coarse particles

Figure 10 shows the profile obtained from a sample consisting of particles of taurine, after carrying out a 1D measurement with a BB optical system. The intensity ratio for the obtained diffraction peaks has no reproducibility, and the intensity ratio of the peaks varies depending on how the sample is selected. This problem become especially conspicuous if the sample size is small and the particles are large. It is evident from a comparison with the standard diffraction pattern of taurine shown in Fig. 11 that it is difficult even to identify the crystal phase.

Figure 12 shows an image obtained via 2D measurement of the taurine in Fig. 10(a) using a 2D slit. It is possible to confirm the spot-shaped 2D diffraction image due to the coarse particles.The measurement range in the 1D measurement is shown with the red box on the 2D diffraction image in Fig. 12. In the case of the 1D measurement, the Debye rings that can be measured at $2\theta=20°$ have only a $\beta=3.8°$ portion of the entire circumference of $\beta=360°$ (in the case of D/teX Ultra 250, with R=300 mm). Therefore, it is easy for peak intensity to be affected by coarse particles. On the other hand, the 2D detector has a broader width in the $\beta$ direction than a 1D detector. It is also possible to change the distance between the sample and detector, and therefore the Debye ring that can be measured at $2\theta=20°$ is broadened to a $\beta=14.6°$ portion (Hypix-400, with R=150 mm). Figure 13 shows a comparison of the standard diffraction pattern with a 1D profile obtained by converting the 2D diffraction image in Fig. 12. In the 1D profile after conversion, agreement with the standard diffraction pattern improved. By using 2D measurement as indicated above, it is possible to visually understand the cause of fluctuation in peak intensity. In addition, broadening the detection range for diffracted X-rays using a 2D detector will likely make it easier to identify the phase of samples composed of coarse particles.

### 3.2. 2D measurement of samples with preferred orientation

Figure 14 shows a comparison of a standard diffraction pattern with a 1D profile of tranexamic acid, an acicular crystal. Peaks are obtained at the standard angles, but the peak intensity ratios do not match. Figure 15 shows the 2D diffraction image for this sample. It can be confirmed that the [0k0] series diffraction image has an arc shape, and the crystals are in the preferred orientation.

This is an example where, by using 2D measurement,

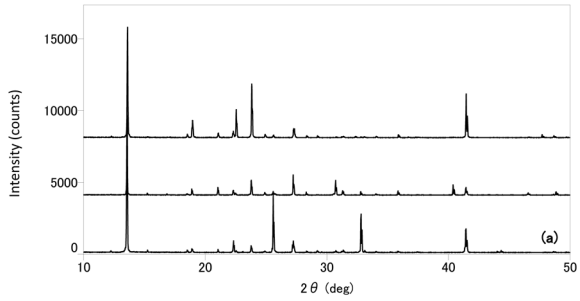


**Fig. 10.** 1D profile obtained through refill measurement of taurine.

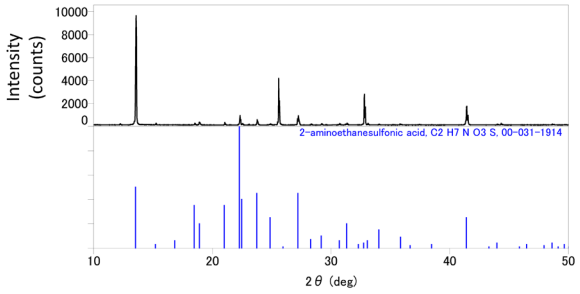


**Fig. 11.** Comparison of profile of taurine in Fig. 10(a) and a standard diffraction pattern.

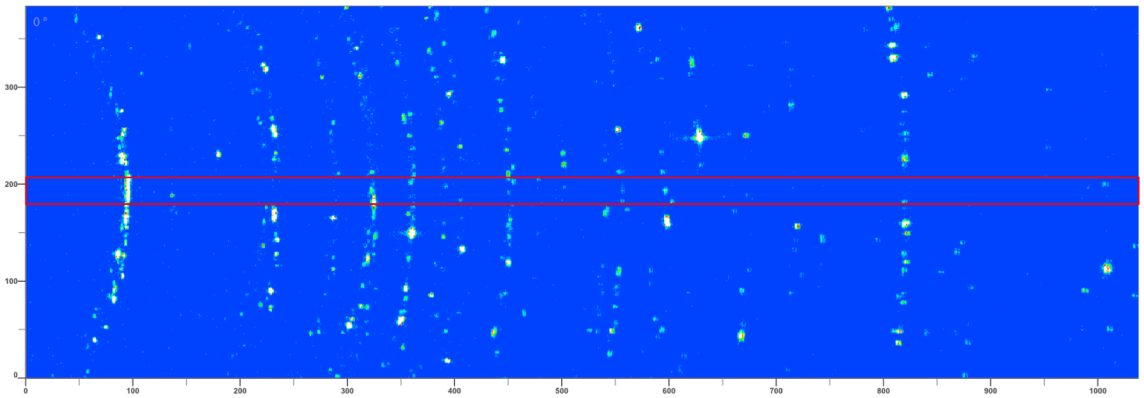


**Fig. 12.** 2D diffraction image of taurine in Fig. 10(a).

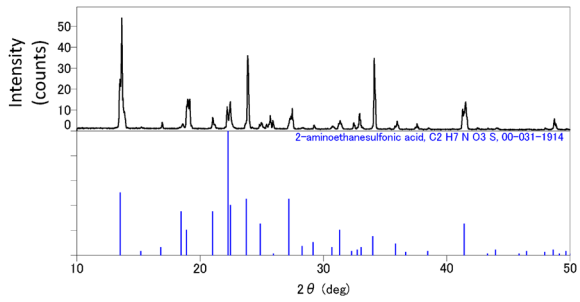


**Fig. 13.** Comparison of 1D converted profile of Fig. 12 and standard diffraction pattern.

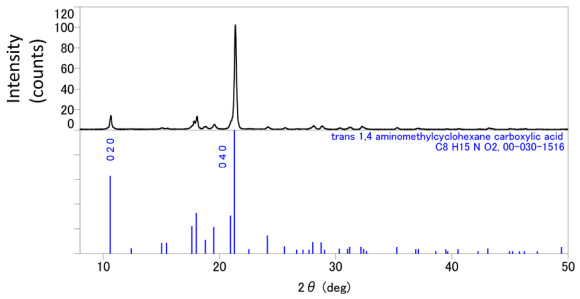


**Fig. 14.** Comparison of 1D profile of tranexamic acid and standard diffraction pattern.

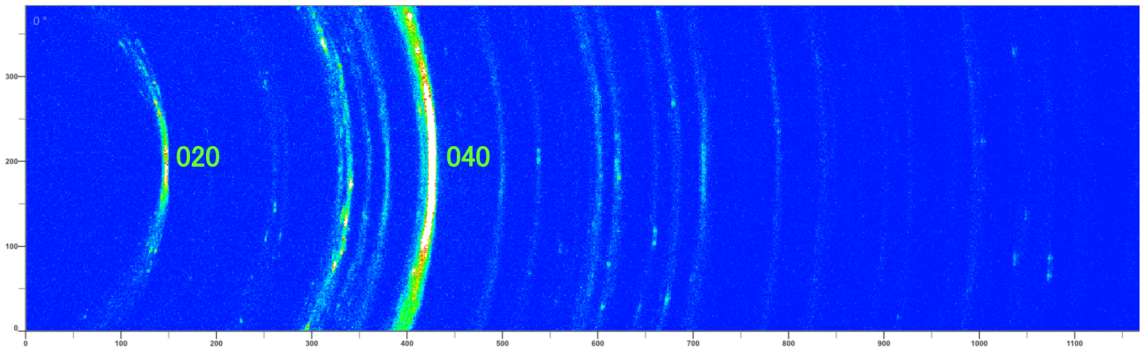


**Fig. 15.** 2D diffraction image of tranexamic acid.

it is possible to visually understand the cause underlying a failure to reproduce the peak intensities of the standard pattern.

## 4. Conclusion

Due to the advent of new optical elements, e.g., detectors enabling multi-dimensional measurement (HyPix series), CBO units equipped with flat multilayer mirrors (CBO-$\alpha$), and 2D slits, it has become possible to easily switch equipment configurations. In this way, it is possible for the person conducting the diffraction experiment to select the optimal measurement dimensionality and optical system to suit the sample condition and purpose. This paper has presented examples where high-speed 1D measurement using the BB method and DB is effective for detecting trace components, and examples where simple 2D measurement is effective for coarse particles and crystallites with a preferred orientation.

## Reference

( 1 ) T. Osakabe: *Rigaku Journal (English version)*, **33** (2017), No. 1, 15−19.