Introduction to powder X-ray diffractometry
I. Overview

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1. Introduction

Until the late 2000s, only scintillation counters (SC) were used as the detectors for general-purpose powder X-ray diffractometers. Thereafter, the core technologies that combine to create an X-ray diffractometer evolved dramatically. A one-dimensional (1D) detector—and subsequently a two-dimensional (2D) detector—came on the market, followed by new optical devices such as multilayer mirrors, in which layering technologies of super-thin film were applied. Analysis software functionality also improved remarkably. For instance, in addition to calculating crystallite size and lattice constants, programs implemented new algorithms and parameters, such as the application of whole pattern fitting[1], the Fundamental Parameter (FP) method[2], consideration of anisotropy[3] and distribution in crystallite size[4].

The 1D and 2D measurement conditions described below are somewhat different from those with an SC. The factors to which we should pay attention have changed when thinking about the optimal conditions to obtain high-quality data. Even in references in which only measurements using the focusing method and a zero-dimensional detector were described, useful hints to obtain high-quality data were rarely discussed. For this reason, in the series of articles making up this basic powder XRD course, we will explain the fundamentals of X-ray diffraction and expertise, sprinkled with the latest applications.

In this overview article, the principles and instruments used in the powder X-ray diffraction method, and what experiments can evaluate, are explained.

2. What the Powder XRD Method Reveals about Powder and Bulk Samples

2.1. Bragg's condition of diffraction

There is a phenomenon called reflection[5] distinct from diffraction. Specifically, strong reflection intensity is observed when incident X-rays impinge at a low angle onto a sample that has a flat and mirror-like surface. As the incident angle increases, the reflection intensity decreases exponentially. However, even for a powder sample that does not have a mirror-like surface, X-rays interfere constructively when the optical path difference of the X-rays reflected by electrons of the first and second layers is equal to an integral multiple of the X-ray wavelength (Fig. 1). Consequently, X-rays are observed only in discrete directions. This phenomenon is called X-ray diffraction, and the directions of X-ray diffraction are defined by Bragg's condition of diffraction as shown in formula (1).

Here, d is the lattice spacing, θ is the incident angle and λ is the X-ray wavelength. Note that the diffracted X-ray wavelength is identical to that of the incident X-rays.

$$2d \sin \theta = n\lambda \quad \cdots\cdots\cdots\cdots\cdots\cdots (1) \text{ (n is an integer)}$$

2.2. Characteristics of the X-ray diffraction method

X-ray diffraction is a method to obtain the crystal structure of a sample. For diamond and graphite (C), or for the rutile and anatase forms of titanium oxide (TiO_2), the chemical formulas are identical in each case, but the crystal structures are different. Therefore, X-ray diffraction profiles allow you to distinguish the former from the latter. Also, suppose there has been a requirement to identify the rust of the corroded part of an iron sample. The X-ray diffraction method allows you to identify iron oxides and hydroxides such as hematite (Fe_2O_3), magnetite (Fe_3O_4), goethite (α-FeOOH) and lepidocrocite (γ-FeOOH). In other words, compounds making up the rust can be identified.

Other advantages of the X-ray diffraction method are listed below.
· It is a non-destructive analysis, which means the sample can be subjected to other analysis after the measurement.
· The sample can be measured in an open-air atmosphere; therefore, sample preparation is very easy.
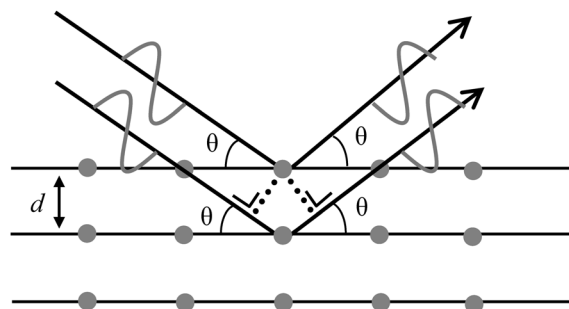· The results from XRD represent average information over the irradiated region of the sample because the

Fig. 1. Bragg's condition of diffraction.

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Table 1.　Evaluation item list in powder X-ray diffraction method.

Evaluation method name	Obtainable information
Qualitative analysis	Identifies compounds by searching for a similar diffraction pattern in a database.
Quantitative analysis	Calculates content percentage of compounds in a sample.
Crystallinity	Calculates the ratio of crystalline component to amorphous component.
Crystallite size analysis (including lattice strain)	Calculates crystallite size, which is the size of one single crystallite constituting a particle. Calculates lattice strain, which is the degree of strain of the crystallites in conjunction with the crystallite size.
Crystal structure analysis (Rietveld analysis)	Evaluates the crystal structure of a sample by refining lattice constants, atomic positions and occupancies and temperature factors of an initial structure model.
in-situ analysis	Collects X-ray diffraction data while simultaneously changing parameters such as temperature, humidity, ambient gas, tension/compression conditions and charge-discharge conditions to evaluate the influence of those parameters.
Particle/pore size analysis[7]	Analyzes particle or pore size and its distribution from the scattering profile in a small angle region. Can analyze amorphous material.
Preferred orientation (texture) analysis[8], [9]	Evaluates crystal orientation and the degree of orientation relative to the directions of the incident X-rays. The incident direction of X-rays against the sample having preferred orientation or texture is changed during the measurement.
Residual stress analysis[10], [11]	Measures residual stress by calculating the peak shift resulting from the distortion of lattice plane distance d due to a compressive or tensile stress. Distances between lattice planes different in direction relative to the sample surface are measured by changing the direction of the incident X-rays.
PDF analysis[12]	Determines atomic distances and the coordination number from the Pair Distribution Function (PDF) profile calculated from a diffraction profile. Can analyze amorphous material, as well.

irradiated diameter is several tens of μm to dozens of square mm.

2.3.　Items characterized in the powder X-ray diffraction method

The X-ray diffraction method is capable of conducting various evaluation functions besides phase identification. A list of evaluations possible with the powder X-ray diffraction method is shown in Table 1. In this list, all the phenomena in the interaction between a sample and X-rays are "diffraction" events except for particle/pore size analysis, which is based on the diffuse scattering phenomenon[6]. In X-ray diffraction, the peak width, position and intensity ratio change according to the lattice constants, crystallite size, residual stress and the atomic positions and occupancies in the crystal structure. This is the reason why X-ray diffraction can be used to analyze various items.

3.　X-ray Diffractometer
3.1.　Configuration of an X-ray diffractometer

An X-ray diffractometer mainly consists of three parts: an X-ray generator (incident side), a goniometer and a detector (receiving side) as shown in Fig. 2. In recent years, most goniometers maintain the sample in a horizontal position. You don't have to worry about spilling powder samples or falling bulk samples when the sample is kept horizontally. In particular, this geometry is very useful for liquid and gel samples, and also powder samples where the grains are coarse, making it difficult to retain them on a sample holder. Because the sample stage at the rotation center of the goniometer can be dismounted, you can conduct various
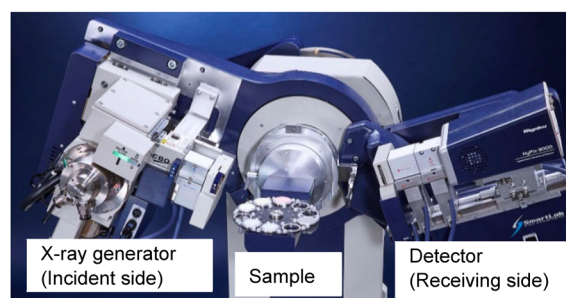
Fig. 2.　X-ray diffractometer.

kinds of characterization by installing parts called "attachments" that add a specific function according to your purpose.

3.2.　Incident side optics

For laboratory use, there are two kinds of X-ray generators available for X-ray diffractometers: sealed tube and rotating anode. Generally, a rotating anode is capable of delivering 5−7 times higher intensity compared to a sealed tube. The collection of higher intensity has an advantage in the detection of trace peaks. This feature also means that you can reach the target intensity (counts) at a higher scan speed; therefore, it allows you to reduce the measurement time.

The SmartLab has a multilayer mirror at the immediate downstream side of the X-ray generator. Various types of mirrors can be mounted according to the desired purpose. This unit is called CBO (Cross Beam Optics)[13]. As of 2020, we have CBO (parallel beam), CBO-α (divergent beam) and CBO-E
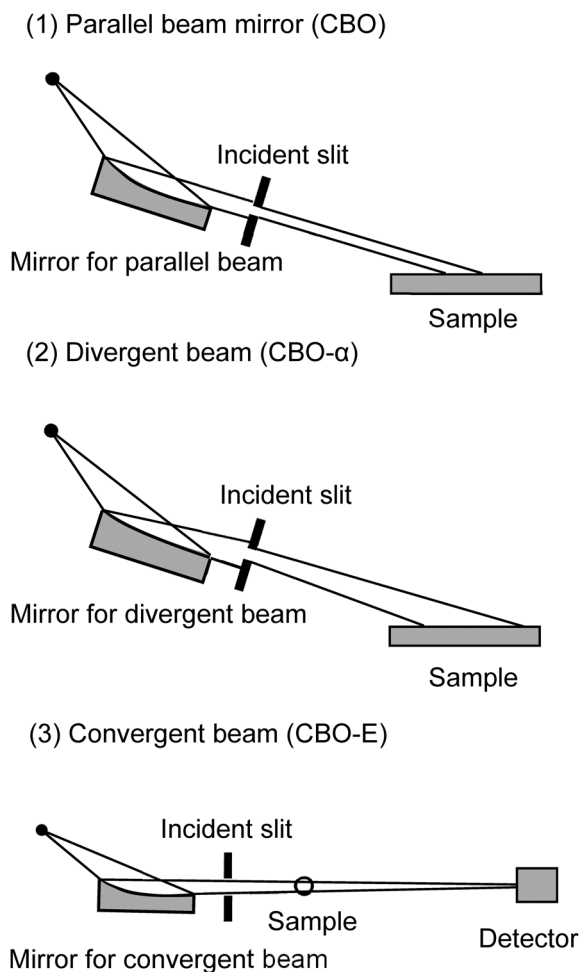
(1) Parallel beam mirror (CBO)

(2) Divergent beam (CBO-α)

(3) Convergent beam (CBO-E)

Fig. 3.   Types of mirror for SmartLab.

(1) zero-dimensional detector

(2) one-dimensional detector

(3) two-dimensional detector

Fig. 4.   Detector and the type of measurement dimension.

(convergent beam). The supported combinations between the beam type and the radiation type are: Cr radiation (parallel), Co and Cu radiation (parallel, divergent, convergent), Mo radiation (parallel, convergent) and Ag radiation (convergent). The differences in the CBO lineups are shown in Fig. 3.

Normally, parallel beam optics can be used for measurements in the reflection method, which detects X-rays diffracted at the sample surface, and the transmission method, which detects diffracted X-rays transmitted through the sample. While a divergent beam is primarily used for the reflection method, the convergent beam is used only for the transmission method. Using the appropriate radiation and optical elements for to the measurement purpose enables you to collect high-quality data.

3.3.   Detectors and the measurement dimension

There are three types of measurement dimensions for X-ray diffraction: zero-dimensional (0D), one-dimensional (1D) and two-dimensional (2D). Because 0D mode has no information about the 2-theta position on the detector surface, only intensity information is obtained regardless of the position where X-rays land, such as the center or the edge of the detector surface. Therefore, a slit typically having the width of 0.15 or
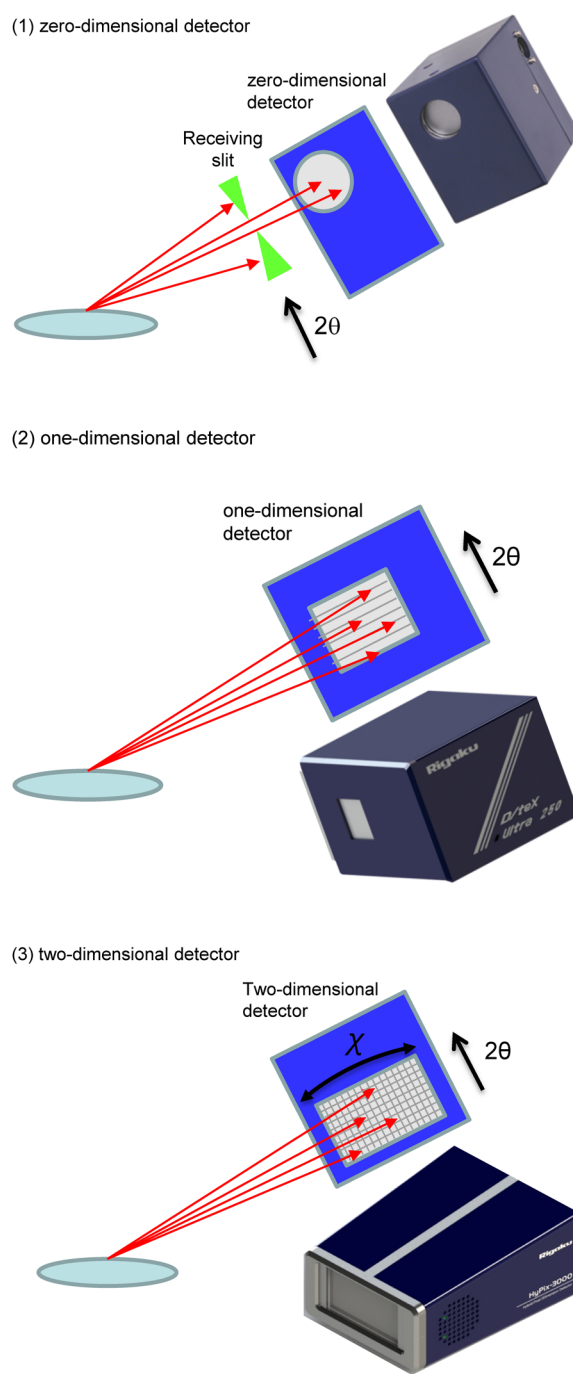
0.30 mm is required in front of the detector to obtain appropriate angular resolution. Each sensor element on a 1D detector surface has a strip shape, and a number of these elements are arranged so that the long direction of the strip is perpendicular to the 2-theta direction. In 1D scan mode, all sensor elements on the detector surface collect intensity one after another for a certain 2-theta position. The 1D measurement does not require a slit to restrict the receiving width because the detector has information about the 2-theta position. The 1D scan mode allows you to obtain tens of times higher intensity compared to the 0D scan because, in principle, the difference in the receiving slit width leads to an

(1) Selection of analysis purpose

(2) Selection of sample type

(3) Offered optics

Fig. 5.   Wizard dialog of SmartLab Studio II.

Fig. 6.   Smart message in optical alignment.

intensity difference[14]. Also, the peak profile collected with the 1D scan has a high angular resolution. The peak width with the 1D scan corresponds to the receiving slit condition of 0.1 mm in the 0D scan mode, assuming the width of one strip against the scan direction is $100\,\mu$m. Today, the 1D scan mode is a de facto standard for the measurement of powder samples.

A 2D detector is composed of square/rectangular pixels around $100\,\mu$m on each side. These pixels are arranged in a matrix in a plane, and the active detection area usable for data collection is larger than that with 0D and 1D detectors. The 2D detector allows you to observe a wider range of a Debye ring directly, and to visually grasp sample conditions such as preferred orientation and coarse grains. In addition, high intensity can be obtained by reducing the absorption of X-rays due to air because the distance between the sample and the detector is shorter than in 0D and 1D mode.

3.4.   Control/Analysis software

Our current program SmartLab Studio II[15] is an "integrated" X-ray analysis software suite. This integrated software has both a measurement part (called a "plug-in") to control an instrument and an analysis plug-in to use after data collection. Therefore, you
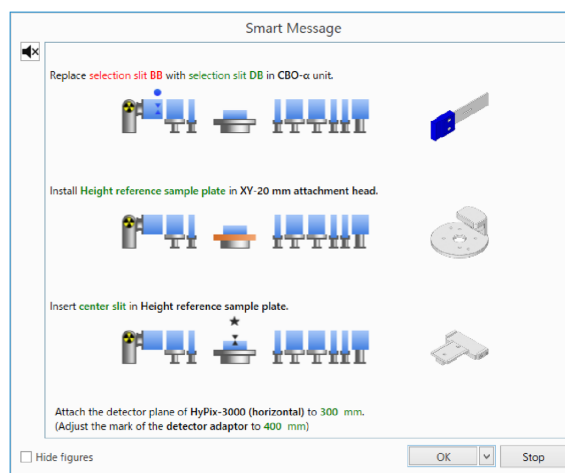
don't need to launch analysis software separately when conducting the analysis. In addition, passing data from the measurement plug-in to the analysis plugin is smooth and convenient. On the other hand, as noted above, new optical devices and detectors are introduced to the market regularly, and instrument configurations can be complicated. To address this issue, SmartLab Studio II has a wizard function. All you need to do is select an evaluation purpose and answer the questions in the wizard form. The system suggests the optimum optics from possible combinations among your optical parts (Fig. 5). Each component of the SmartLab has a photo-reflector that stores identifying information that is read to recognize which devices are currently mounted on the instrument. If a sequence consisting of both optics alignment and data measurement has been prepared in advance (by an expert user), all that you have to do is to run the sequence and follow the message(s) that will instruct you to change optical devices if needed (Fig. 6).

4.   Powder and Bulk Materials Frequently Measured on an X-ray Diffractometer and Applicable Evaluation Items

A wide range of materials can be measured with an X-ray diffractometer. Based on the author's experiences, a list of powder and bulk materials that are frequently measured on an X-ray diffractometer and the applicable evaluation items is shown in Table 2. It is natural that items related to the property and performance of each material are frequently evaluated. In Table 2, the "Qualitative analysis" row includes the simple check of a profile pattern. The "Quantitative analysis" row indicates quantification of crystalline phases, and the quantification of the amorphous component is included in "Crystallinity." "Crystal information" indicates the calculation of the d value without using an initial structure model. Regardless of samples, it is usual to check the diffraction pattern first if the measurement is not for quality control.

It is possible to conduct quantitative analysis

Table 2. Powder and bulk materials that are frequently measured in X-ray diffractometer and the applicable evaluation item.

Samples	Qualitative analysis	Quantitative analysis	Crystallinity	Crystallite size	Crystal information	Refined crystal structure analysis	in-situ analysis	Particle/pore size analysis	Preferred orientation (Texture) analysis	Residual stress	PDF analysis
Pharmaceutical compound	○	○	○	△	—	○	○	—	△	—	△
Ink materials	○	△	—	—	—	—	—	○	—	—	—
Liquid crystal	○	—	—	—	○	—	○	—	○	—	—
Paper and pulp	○	○	△	—	—	—	—	—	—	—	—
Environmental dust	○	○	—	—	—	—	—	—	—	—	—
Metal complex	○	—	—	△	○	○	○	△	—	—	—
Light metal materials	○	△	—	—	—	—	○	—	○	○	—
Mineral	○	○	△	—	△	○	△	—	—	—	—
Catalyst	○	—	—	○	—	○	○	○	—	—	○
Food materials	○	△	○	—	△	—	○	○	○	—	—
Magnetic materials	○	—	—	○	—	○	△	△	○	○	—
Slug	○	○	△	—	—	—	—	—	—	—	—
Cutting tools	○	—	—	—	—	△	△	—	○	○	—
Cement	○	○	○	—	—	○	△	—	—	—	—
Ceramics	○	○	△	△	—	○	○	—	△	○	○
Fibers	○	—	○	△	△	—	△	○	○	—	—
Steel materials	○	○	—	○	—	○	△	—	○	○	—
Positive electrode materials	○	△	—	△	—	○	○	—	—	—	○
Anode electrode materials	○	—	—	○	—	○	○	○	—	—	○
Nano particles	○	—	—	○	—	—	△	○	—	—	○
Polymer	○	—	○	△	△	—	△	○	○	—	—
Plating film	○	—	—	○	—	—	—	—	○	○	—
Dielectric materials	○	○	○	△	—	○	○	○	△	○	△
Grease	○	—	○	△	△	—	○	—	△	—	—

○　Frequently evaluated

△　Occasionally evaluated

—　Rarely evaluated

when multiple phases are contained in the sample. In this case, a powdered form is preferable to obtain a correct quantitative value. When crystal phases are homogeneously distributed in the X-ray penetration depth in the bulk form sample, it is possible to perform quantitative analysis. However, one should note that layers closer to the sample surface give higher quantitative values due to the influence of X-ray absorption when the sample has a layer structure. Preferred orientation (texture) and residual stress analysis are often the focuses in bulk samples.

5.　Conclusion

In this article, the principle, instrument and applicable evaluation items of the powder X-ray diffraction method were briefly described. In the second and subsequent articles, we are planning to describe the measurement conditions to collect high-quality data, and then the measurements in Table 1, principles of analyses, expertise, critical points and application examples on qualitative analysis, quantitative analysis, crystallinity analysis, crystalline size analysis, crystal structure analysis, in-situ analysis and particle/pore size analysis.

References

(1) G. S. Pawley: *J. Appl. Cryst*., **14** (1981), 357−361.

(2) R. W. Cheary and A. Coelho: *J. Appl. Cryst*., **25** (1992), 109−121.

(3) P. Scardi and M. Leoni: *J. Appl. Cryst.*, **32** (1999), 671−682.

(4) J. I. Langford and A. J. C. Wilson: *J. Appl. Cryst*., **11** (1978), 102−113.

(5) M. Yasaka: *Rigaku Journal (English version)*, **26** (2010), No. 2, 1−9.

(6) R. I. Barabash, G. E. Ice and P. E. A. Turchi: *Diffuse Scattering and the Fundamental Property of Materials,* (2009), Momentum Press.

(7) A. Sasaki: *Rigaku Journal (English version)*, **22** (2005), No. 1, 31−38.

(8) K. Nagao and E. Kagami: *Rigaku Journal (English version)*, **27** (2011), No. 2, 6−14.

(9) K. Nagao and A. Sasaki: *Rigaku Journal (English version)*, **35** (2019), No. 2, 1−7.

(10) U. Welzel, J. Ligot, P. Lamparter, A. C. Vermeulen and E. J. Mittemeijer: *J. Appl. Cryst*., **38** (2005), 1−29.

(11) A. Nezu, H. Matsuzaka and R. Yokoyama: *Rigaku Journal (English version)*, **30** (2014), No. 2, 4−12.

(12) M. Yoshimoto and Y. Shiramata: *Rigaku Journal (English version)*, **36** (2020), No. 1, 10−18.

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

(14) Y. Namatame, T. Kuzumaki, Y. Shiramata and K. Nagao: *Rigaku Journal (English version)*, **34** (2018), No. 1, 9−13.

(15) *Rigaku Journal (English version)*, **31** (2015), No. 2, 25−26.