# Powder X-ray Diffraction Basic Course Fifth Installment: Quantitative analysis

# Takahiro Kuzumaki\*

#### Abstract

Powder X-ray diffraction is widely used as an analytical method to evaluate various crystalline materials. This paper describes the basics and evaluation examples of the RIR (Reference Intensity Ratio) method and the Rietveld method.

In the RIR method, quantitative analysis is performed based on the integrated intensity of diffraction peaks and the RIR values registered in databases. In this method, rapid quantitative analysis is performed once qualitative analysis has been completed. However, if the peak intensity ratio differs from that in the database due to preferred orientation or other reasons, the obtained quantitative values will be inaccurate.

The Rietveld method is a method for refining crystal structure parameters by fitting a calculated pattern obtained from lattice parameters, crystal system, atomic coordinates, etc., to a measured diffraction pattern using the least-squares method. The obtained scale factor and information about the crystal structure can be used for quantitative analysis. The Rietveld method enables accurate quantitative analysis even if samples have preferred orientation and/or complex diffraction patterns.

The combination of the Rietveld method with the internal standard method, known as the PONKCS (partial or no known crystal structure) method, and the RIR method also enable quantitative analysis of amorphous phases.

#### 1. Introduction

In Part 4 of the Basic Course on Powder X-ray Diffraction Methods, "Qualitative Analysis" was described<sup>(1)</sup>. In Part 5, "Quantitative Analysis" will be explained.

Powder X-ray diffraction is widely used as an analytical method for various crystalline materials. Since the properties and functions of materials often depend on included crystalline phases and their quantity ratios, quantitative analysis by powder X-ray diffraction is widely used from research and development to quality control.

The classical quantitative analysis method in powder X-ray diffraction is the calibration curve method. This method uses the correlation between the crystalline phase content and the X-ray diffraction intensity. In general, the integrated intensity of the highest peak of the phase of interest that does not overlap with peaks of other coexisting phases is used for quantification, thus minimizing error factors and enabling accurate quantification.

However, the use of the calibration curve method has decreased in recent years for the following reasons: (1) pure material of the phase of interest is required for the preparation of the calibration curve, (2) preparation of samples for the calibration curve is time-consuming, and (3) the quantification error increases when the peaks of the phase of interest overlap those of other co-existing phases. In this paper, the RIR method<sup>(2)</sup> (or RIR quantitation) and the Rietveld method<sup>(3)</sup> are described. These methods are standardless quantitative analysis methods that do not require reference materials.

With them, accurate quantitative analysis is also possible even when the diffraction peaks of the phase of interest and other phases overlap. Another quantitative analysis method based on pattern fitting is the DD (Direct Derivation) method. This quantitative analysis method is described in detail in references (4), (5), so please refer to them if necessary. In quantitative analysis, it is very important to improve the quality of the acquired data. refer to Refs. (6), (7).

#### 2. Quantitative Analysis using the RIR Method

The RIR method, a standardless quantitative analysis method, is based on the integrated intensity of the highest diffraction peak and the RIR value of each phase registered in a database, etc. The RIR value is defined as the intensity ratio of the highest peak of corundum vs. that of the crystalline phase when corundum is mixed with the same amount as the crystalline phase in question. Normally, the integrated intensities of diffraction peaks are used in quantitative analysis, but the diffraction peak intensities are different for different crystals due to different atomic scattering factors. By using the RIR value, the ratio of diffraction peak intensities between crystalline phases can be converted to a mass fraction, allowing quantitative analysis. The equation of the RIR method is shown as follows.

$$W_i \propto \frac{I_i^{\max}}{R_i} \tag{1}$$

 $W_i$  is the mass fraction of an analytical phase *i*,  $I_i^{\text{max}}$  is the highest peak intensity, and  $R_i$  is the RIR value. For  $I_i^{\text{max}}$ , the integrated intensity of the diffraction peak with the highest intensity is usually selected, but

<sup>\*</sup> Global Product Marketing Dept., Product Division, Rigaku Corporation.

RIR Quantification ? 4					ų				
Da	Dataset: Mix2 🗹 🗹 Reflect to all								
	Peak	2 <del>0</del> , °	Int. I., cpsº	Anatase	Rutil	e			
•	1	25.244(5)	4170(46)	<b>1</b> 01					^
	2	27.372(3)	1137(14)		110				
	3	36.019(3)	489(7)		101				
	4	36.879(7)	224(4)	103					
	5	37.736(3)	894(8)	004					
	6	38.502(4)	271(4)	112					
	7	39.116(3)	76(2)		200				
	8	41.172(3)	242(4)		111				
	9	43.987(4)	85.8(19)		210				
	10	47.9755(16)	1249(8)	200					
	11	53.8366(18)	780(7)	105					
	12	54.2652(14)	681(7)		211				
	13	55.002(2)	790(6)	211					
	14	56.572(4)	209(4)		220				
	15	62.060(6)	128(3)	213					
	16	62.640(2)	727(5)	204	002				
	17	63.994(4)	95(2)		310				
	18	67.687(12)	3.6(10)						~
RIR Value Settings									
D	ataset /	Weight Fractio.	Value, Unit	Anat	ase		Rutile		
М	ix2		0	72.8(3)		27.2(3	3)		

Fig. 1. Peak selection dialog box in SmartLab Studio II for RIR quantification.



Fig. 2 Diffraction peaks used for quantitative analysis of simulated sample A by the RIR method.

 Table 1
 Quantitative values (mass %) for each phase using the RIR method and amount of added (mass %) of each phase of simulated sample A.

Phase	Quantitative values	Amount added
Rutile	33.1	33.3
Anatase	34.5	33.3
Periclase	32.4	33.3

if the highest peak overlaps with the peaks of other phases, the second or third highest peak can be selected. Currently, RIR values are obtained experimentally and computationally for a wide variety of materials and are compiled in databases; for example, from ICDD.

Figure 1 shows the peak selection dialog box in SmartLab Studio II for RIR quantification.

The advantage of RIR quantification is that rapid quantitative analysis can be performed as soon as the qualitative analysis is completed. If the RIR value is listed on the card selected for qualitative analysis, it can be quantified at the touch of a button. Figure 2 and Table 1 show the results of RIR quantification using a sample (simulated sample A) that is a mixture of equal amounts of rutile  $(TiO_2)$ , anatase  $(TiO_2)$ , and periclase (MgO).

This simulated sample has no peak overlap and no preferred orientation, thus accurate quantitative analysis is possible. However, it is difficult to perform correct RIR quantification when the peak intensity ratios differ from those in the database due to preferred orientation, or when peaks cannot be decomposed due to peak overlap. For such samples, quantitative analysis by the Rietveld method described in the next section is suitable.

#### 3. Quantitative Analysis using the Rietveld Method

The Rietveld method is a method for refining crystal structure parameters by fitting a calculated pattern obtained from lattice parameters, crystal system, atomic coordinates, etc., to a measured diffraction pattern using the least-squares method. The calculation is performed to minimize the weighted residual sum of squares S(x).

$$S(x) = \sum_{i} \frac{1}{\sigma(y_{i})^{2}} \left[ y_{i} - f_{i}(x) \right]^{2}$$
<sup>(2)</sup>

where  $y_i$  is the measurement intensity,  $\sigma(y_i)$  is the intensity error estimated by counting statistics, and  $f_i$  is the intensity calculated by the following equation.

$$f_{i}(x) = sS_{R}(\theta_{i})A(\theta_{i})D(\theta_{i}) \sum_{k} m_{k}|F(h_{k})|^{2}$$

$$P_{k}LP(\theta_{k})G(\Delta 2\theta_{ik}) + y_{b} (2\theta_{i})$$
(3)

where s is the scale factor,  $S_{R}(\theta_{i})$  is the surface roughness correction factor,  $A(\theta_i)$  is the absorption factor,  $D(\theta_i)$  is the irradiation width correction factor,  $m_k$  is the multiplicity of the Bragg reflection, F is the crystal structure factor,  $h_k$  is the diffraction index *hkl*,  $P_k$ is the selected orientation function,  $LP(\theta_k)$  is the Lorentz polarization factor,  $G(\Delta 2\theta_{ik})$  is the profile function, and  $y_b(2\theta_i)$  is the background intensity. If a sample contains multiple crystalline phases, refinement is performed for each phase to optimize the scale factor, peak positions and shapes to make the calculated pattern as close to the measured pattern as possible. Since the refined scale factor is proportional to the content of each phase, the following equation can be used for quantitative analysis by using the scale factor and information about the crystal structure.

$$W_i = \frac{s_i Z_i M_i V_i}{\sum_j s_j Z_j M_j V_j} \tag{4}$$

where  $W_i$  is the mass fraction of analyte phase *i*, *s* is the scale factor, *Z* is the number of chemical formulas in the unit cell, *M* is the molecular mass of the formula, and *V* is the volume of the unit cell. In SmartLab Studio II, the crystal structure parameters are converted to RIR values using equation (5) and then used for quantitative analysis.

$$R_{i} = \frac{I_{i}^{max} Z_{c} M_{c} V_{c}}{I_{c}^{max} Z_{i} M_{i} V_{i}}$$

$$\tag{5}$$



Fig. 3. Diffraction peaks used for quantitative analysis of simulated sample B using the RIR method.



Fig. 4. Profile fitting results of simulated sample B using the Rietveld method.

Table 2.Comparison of analysis results (mass%) between<br/>the RIR and Rietveld methods using simulated<br/>sample B.

Phase	Analysis values (RIR method)	Analysis values (Rietveld method)	Amount added
Rutile	30.4	33.8	33.3
Anatase	29.7	32.5	33.3
Calcite	39.9	33.7	33.3

where  $R_i$  is the RIR value of analytical phase *i*,  $I_i^{max}$  is the maximum peak intensity of analytical phase *i*, and the subscript *c* refers to the value for corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>). Therefore, SmartLab Studio II can perform quantitative analysis based on the *d*–*I* list and RIR value of an entry in a powder diffraction database card even if the crystal structure is not available.

In contrast to the RIR method, quantitative analysis by the Rietveld method can be applied to samples with many overlapping diffraction peaks of multiple phases. Preferred orientation can also be corrected using the March–Dollase function<sup>(8)</sup> and the spherical harmonic function<sup>(9)</sup>. To compare the quantitative result obtained using the RIR method with that using the Rietveld method for samples with preferred orientation, a sample (simulated sample B) containing equal amounts of rutile, anatase, and calcite (CaCO<sub>3</sub>) is analyzed. Figure 3 shows the diffraction peaks used in the calculation of the RIR method for the quantification of simulated sample B, Figure 4 shows the profile fitting results using the Rietveld method, and Table 2 shows a comparison of the



Fig. 5. Profile fitting results of NIST2687 using the Rietveld method.

Table 3. Rietveld analysis results and certified values (mass%) of NIST 2687.

Phase	Analysis values	Certified values
Alite	71.4	$71.27 \pm 1.27$
Belite	12.3	$12.57 \pm 1.22$
Aluminate	12.2	$11.82 \pm 1.03$
Ferrite	3.3	$2.81\!\pm\!0.68$
Arcanite	0.8	$0.92 \!\pm\! 0.15$

analysis results between the RIR and Rietveld methods.

The peak intensity derived from the 104 reflection of calcite is higher due to preferred orientation, so the RIR method, which uses a single peak, causes a large quantitation error for crystalline phases with preferred orientation. The standardless quantitative method calculates the sum of each crystalline phase to be 100%, so the quantification error extends to other phases as well. In contrast, the Rietveld method allows a correction for preferred orientation so that more correct quantitative values can be obtained. However, the preferred orientation correction should be used only for crystalline phases with known preferred orientation planes. If there is a large difference between the calculated and measured patterns in the absence of a phase with preferred orientation, there may be an unidentified crystalline phase or the initial structural model may be incorrect. Note that using a preferred orientation correction only to reduce the residuals may result in inaccurate evaluation.

The Rietveld method is widely used in industry—for quality control in cement plants, for example. Clinker, the raw material of cement, contains alite, belite, aluminate, and ferrite as the main phases. These phases show complex diffraction patterns and many peaks overlap. Therefore, quantitative analysis by calibration curves or RIR methods are difficult. Figure 5 shows the quantitative analysis results of the NIST clinker sample. Table 3 shows the Rietveld analysis results and certified values.

Even for samples with complex diffraction patterns, such as cement samples, correct quantitative analysis can be performed.

 $R_{\rm wp}$ ,  $R_{\rm p}$ ,  $R_{\rm e}$ , and S are often used as indicators to evaluate the correctness of a Rietveld analysis, and are

**Table 4.** Targeted value of  $R_{wp}$  after analysis is completed.

Sample type	Target $R_{wp}$ (%)
Normal sample	Around 10.0-15.0
High background sample	Around 5.0–10.0
Low crystallinity sample	Around 7.0–13.0
High crystallinity sample	Around 15.0-20.0

given by the following equations.

$$R_{wp} = \sqrt{\frac{\sum_{i} w_i \left( y_i - f_i(x) \right)}{\sum_{i} w_i y_i^2}} \tag{6}$$

$$R_{p} = \sqrt{\frac{\sum_{i} \left| y_{i} - f_{i}\left(x\right) \right|}{\sum_{i} y_{i}}} \tag{7}$$

$$R_e = \sqrt{\frac{N-P}{\sum_i w_i y_i^2}} \tag{8}$$

$$S = \frac{R_{wp}}{R_e} \tag{9}$$

where  $w_i$  are the statistical weights, N is the number of total data points, and P is the number of parameters to be refined.

 $R_{wp}$  is the most common *R* factor used in Rietveld analysis and indicates the weighted agreement including background intensity. However, the values of  $R_{wp}$ and  $R_p$  vary depending on the background intensity and diffraction intensity. Therefore, *S* is used as a parameter to compare  $R_{wp}$  with  $R_e$ , which represents the statistically expected ideal  $R_{wp}$ . *S* is often used as a substantial indicator of good fit, and a value of *S* close to 1 indicates that the refinement was performed properly. Table 3 shows the targeted values of  $R_{wp}$  for each sample type. It should be used as a reference for analysis.

An analysis result is considered be satisfactory if S is smaller than 1.3<sup>(10)</sup>. However, in quantitative analysis using the Rietveld method for samples containing multiple crystalline phases, the analysis result is often higher than 1.3. In the author's experience, even with an S value of about 2.0, appropriate results are often obtained if the residual profile confirms that there are no problems. These indices are indicators of the degree of fit, but even when the values are sufficiently low, the analyzed parameters may converge to physically inappropriate values. For correct quantitative analysis, it is important not only to check the R factor and S value, but also to check the degree of agreement between the calculated and measured patterns for each phase, and confirm that the quantitative results are consistent with the elemental analysis results.

# 4. Quantitative Analysis of Amorphous Phases using the Rietveld Method

The quantitative analysis described in the previous section mainly focused on crystalline phases, but quantitative analysis of non-crystalline materials (amorphous phases), is also possible. If an amorphous phase is derived from the same substance as the crystalline phase, it is possible to calculate the degree of crystallinity using the integrated intensity ratio of the diffraction peaks of the crystalline phase and the broad pattern (called a halo) of the amorphous phase after peak decomposition. However, if the amorphous phase is derived from a material different from the crystalline phase, quantitative analysis of the amorphous phase is difficult based on peak intensity only. For such samples, it can be performed by combining the Rietveld method with other methods. The internal standard method<sup>(11)</sup>, the PONKCS (Partial Or No Known Crystal Structure) method<sup>(12)</sup>, and the RIR method are all incorporated in SmartLab Studio II. These methods are hereafter referred to as the "internal standard/Rietveld method," "PONKCS/Rietveld method," and "RIR/Rietveld method," respectively. In the internal standard/Rietveld method, the amorphous phase content is calculated indirectly from the difference between the amount of internal standard mixed in the sample and the Rietveld analysis results. In contrast, the PONKCS/Rietveld and RIR/ Rietveld methods can directly quantify the content of the amorphous phase by setting a virtual crystal structure and RIR value, respectively, to the halo derived from the amorphous phase. This section describes the principle of these methods with analysis examples.

# 4.1 Amorphous phase content determination using the internal standard/Rietveld method

In the internal standard/Rietveld method, a known amount of a crystalline material is added and mixed with the sample as an internal standard, and the measurement data of the mixture containing the internal standard is analyzed by the Rietveld method. The quantitative value of the internal standard is obtained without taking into account the amount of the amorphous phase. If the sample contains an amorphous phase, the calculated amount of the amorphous phase becomes higher than the amount actually added. This is considered to be the effect of the amorphous phase, and the content of the amorphous phase is calculated indirectly using the following equation.

$$C_{i} = \frac{X_{i} \times 100}{C_{STD}^{'}} \times C_{STD}$$
(10)

$$C_A = 100 - C_{\text{STD}} - \Sigma C_i' \tag{11}$$

From equations (10) and (11), the amorphous mass fraction  $C_A$  is calculated as the mass fraction (mass%) of the remainder containing the amorphous phase, where  $C_{\text{STD}}$  is the mass fraction of the added internal standard (mass%),  $C'_{\text{STD}}$  is the quantitative value of the internal standard obtained by the Rietveld method (mass%), and *Ci* is the quantitative value of the crystalline phase obtained by the internal standard method (mass%).

The internal standard material should satisfy the following conditions—be stable at room temperature



**Fig. 6.** Fitting results of simulated sample C by the Rietveld method.

 Table 5.
 Results of amorphous quantification (mass%) by the internal standard/Rietveld method using simulated sample C.

Phase	Analysis values	Amount added
Rutile	20.2	20.0
Anatase	19.4	20.0
Amorphous silica	60.4	60.0

and pressure, not contained in the crystalline phases constituting the sample to be tested, have absorption coefficients of the sample of interest and the internal standard that are close, and should not alter the other phases due to mixing. For example, corundum is often used as an internal standard material added to cement materials<sup>(13)</sup>. The concentration of the internal standard varies, but generally 10 to 20 mass% is added<sup>(14)</sup>. Simulated sample C containing 60.0 mass% amorphous silica, and an equal amount of rutile and silica was used for amorphous determination by the internal standard/ Rietveld method (Fig. 6, Table 5). Corundum was added to simulated sample C as the internal standard at 10.0 mass%.

This method has been used classically, but as mentioned above, sample preparation is complicated because an internal standard must be mixed with the sample. Therefore, in recent years, the PONKCS/ Rietveld and RIR/Rietveld methods, standardless methods that are described in the next chapter, are more popular for the quantification of amorphous phases.

# 4.2 Amorphous quantification using the PONKCS/Rietveld method

The PONKCS/Rietveld method allows quantitative analysis of amorphous phases by assigning a virtual crystal structure to the halo during quantitative analysis by the Rietveld method. The crystal structure parameters to be set are Z (the number of chemical formulas in the unit cell), M (the molecular mass of the formula), and V (the volume of the unit cell).

In this analysis method, first, a pure material with 100% amorphous phase is measured to obtain a measured pattern. Next, lattice constants are assigned to the measured patterns, and V is calculated by profile fitting using the Pawley<sup>(15)</sup> method or other methods.



Fig. 7. Fitting results of simulated sample C by PONKCS/ Rietveld method.

 
 Table 6.
 Results of amorphous quantification (mass%) by the PONKCS/Rietveld method using simulated samples C, D, and E.

Contents of amorphous silica	Analysis values
40.0	40.3
50.0	50.3
60.0	59.6

Finally, profile fitting is performed on the measured data of a mixed sample with a known amount of amorphous phase using the structural model of the amorphous phase for which V is set, and the value of ZM is determined. Once the crystal structure model of the amorphous phase is determined, this model can be applied to samples with the same amorphous phase, thus enabling rapid evaluation of the sample with the amorphous phase. In addition to simulated sample C, amorphous silica was mixed with a sample that is equal amounts of rutile and anatase at 40.0 mass% (simulated sample D) and 50.0 mass% (simulated sample E) to determine the amorphous content using the PONKCS/Rietveld method (Figure 7, Table 6).

In Rietveld analysis, the quantitative values obtained depend on the analysis conditions, and the quantitative results often differ depending on the analysis method, even for the same measurement data. By using the analysis template (preset conditions), Rietveld analysis can start from the same initial values and conditions. The amount of amorphous silica added to each sample and the quantitative values obtained by Rietveld analysis were in very good agreement, as shown in Tables 5 and 6.

## 4.3 Amorphous quantification using the RIR/ Rietveld method

In the RIR/Rietveld method, the RIR value is assigned to the amorphous phase and the following equation can be used for amorphous quantification.

$$W_A = \frac{S_A / R_A}{\sum S_j / R_j} \tag{12}$$

where  $W_A$  is the mass fraction of the amorphous phase,  $S_A$  is the scale factor obtained using Rietveld analysis, and  $R_A$  is the RIR value of the amorphous phase. In this method, as in the PONKCS/Rietveld method, the

RIR values of the amorphous phase are experimentally determined using a mixed sample with a known amount of amorphous phase. Once the RIR value of the amorphous phase is determined, accurate and rapid evaluation of the sample of interest. For examples of actual evaluations of this method, please refer to Refs. (16), (17).

# 5. Conclusion

In the fifth part of the Basic Course on Powder Analysis, methods for quantitative analysis were explained and evaluation examples described. In quantitative analysis by the Rietveld method, preferred orientation can be corrected, and quantitative analysis is possible even when peaks are so closely overlapped that peak decomposition is very difficult or even impossible. It is also possible to quickly quantify the content of the amorphous phase. To perform accurate quantitative analysis, it is necessary to obtain highquality measurement data. If the qualitative analysis is not performed correctly, the results of the subsequent quantitative analysis will also be incorrect. Please refer to Part 2 "Selection of Instrument Configuration," Part 3 "Sample Preparation and Scanning Conditions," and Part 4 "Qualitative Analysis" in conjunction with this article.

#### References

- (1) M. Kasari: *Rigaku Jornal*, **38** (2022), No. 1, 7–12.
- (2) F. H. Chung, R. W. Scott: J. Appl. Cryst., 6, 225-230 (1973).
- (3) H. M. Rietveld : J. Appl. Cryst., 2 (1969) 65–71.
- (4) H. Toraya: Rigaku Journal, **34** (2018), No. 1, 3–8.
- (5) H. Toraya: Rigaku Journal, 35 (2019), No. 2, 27–34.
- (6) M. Omori: Rigaku Journal, **37** (2021), No. 1, 12–19.
- (7) M. Omori: *Rigaku Journal*, **37** (2021), No. 2, 21–25.
- (8) W.A. Dollase: J. Appl. Cryst., **19** (1986), 267–272.
- (9) M. Järvinen: J. Appl. Cryst., **26** (1993), 525–531.
- (10) R. A. Young, *The Rietveld Method* ed. By R. A. Young, Oxford Univ. Press, Oxford (1993), Chap. 1.
- (11) R. C. Jones, C. J. Babcock, W. B. Knowlton : Soil Sci. Soc. Am. J., 64 (2000), 1100–1108.
- (12) N. V. Y. Scarlett, I. C. Madsen : Powder Diffr., 21 (2006), 278– 284.
- (13) T. Sagawa and T. Nawa: *Cement Science and Concrete Technology*, **68** (2014), 46–52.
- (14) A. Ohbuchi, Y. Yamada, H. Asakura, I. Tomatsu, M. Murata, J. Tech. Assoc. Refract. Jpn., 35 (2015) 250–256.
- (15) G. S. Pawley: J. Appl. Cryst., 14 (1981), 357–361.
- (16) A. Ohbuchi, T. Kuzumaki and T. Nakamura: *Bunseki Kagaku*, 68 (2019), 609–614.
- (17) A. Ohbuchi, T. Kuzumaki, M. Kasari, T. Ozawa: *Rigaku Journal*, 38 (2022), No. 2, 1–6.