A new method for quantitative phase analysis: Direct derivation of weight fractions from observed intensities and chemical composition data of individual crystalline phases

Hideo Toraya*

1. Introduction

characterizing multi-component In materials, constituent crystalline phases are first identified, and their relative abundances are quantified, in general, as a second step. Techniques of quantitative phase analysis (QPA) using the X-ray powder diffraction method have been used widely for materials characterization in research and development as well as in quality control of industrial products. Various techniques for QPA have been proposed since about 80 years ago^{(1), (2)}. At present, certain techniques are specialized for QPA of specific materials, such as monoclinic-tetragonal Y-doped $ZrO_2^{(3)}$, $\alpha - \beta$ type Si₃N₄⁽⁴⁾ etc., while other techniques have been used widely for QPA of general materials. In the latter category, the internal standard method using calibration curves⁽⁵⁾, the Reference Intensity Ratio (RIR) method^{(6), (7)} and the Rietveld method^{(8)–(11)} may be listed as major QPA techniques. As is well known, the internal standard method requires experimental procedures to draw the calibration curve, while the accuracy of the method in QPA is considered to be relatively high. Since single peak intensities and database-stored RIRs are used in the RIR method, it is less of a burden to conduct the experiment and data analysis, while the accuracy in QPA depends simply on the accuracy of the measured single peak intensity. The Rietveld method⁽⁸⁾ uses crystal structure parameters in calculating powder diffraction patterns for the least-squares fitting, and this structureconstrained model exhibits its advantage in QPA using the intensity data of complicated powder diffraction patterns like those of cements. Moreover, intensity data of total diffraction patterns are used, and the accuracy in QPA is also considered to be relatively high. The Rietveld QPA technique, however, cannot be applied when crystal structure parameters are not available, and some techniques like the PONKCS (Partially Or Not Known Crystal Structure) method⁽¹²⁾, which compensate for the disadvantages of Rietveld QPA, have been proposed. The PONKCS method can be applied to mixtures consisting of known structure and unknown structure components.

A new method for QPA, called the Direct Derivation (DD) method⁽¹³⁾⁻⁽¹⁵⁾, has recently been proposed. Weight fractions of individual crystalline phases can be derived

from sets of integrated intensities collected in a wide 2θ range, together with chemical composition data. In deriving weight fractions from observed intensities, QPA techniques, which have been proposed until now, use crystallographic information such as a calibration curve, RIR, crystal structure parameters, all of which are derived by diffraction experiments. The DD method uses only chemical information: the chemical composition data. When individual crystalline phases in the mixture are identified, then we will know, in most cases, their chemical compositions. Therefore, the DD method can be applied to most materials, irrespective of whether the crystal structure of the target component material is known or unknown. Even the unknown phase can be quantified, if its chemical composition can be estimated. Moreover, the DD method can be applied to materials, even when the chemical compositions of individual phases are indefinite, such as natural products, some industrial products like cements and slugs etc. The accuracy in OPA is comparable to that obtained by Rietveld QPA. In the following, the theory of the DD method and some examples of its application are presented.

2. Theory

2.1. Intensity-Composition formula

The optical system of conventional-type powder diffractometers most often used in X-ray laboratories, is based on Bragg–Brentano geometry, and in this case, the integrated intensity I_{jk} of the *j*th reflection of the *k*th component in a *K*-component mixture is given by⁽¹⁶⁾.

$$I_{jk} = I_0 \frac{QV_k}{\mu U_k^2} \frac{1 + \cos^2 2\theta_{jk}}{2\sin \theta_{jk} \sin 2\theta_{jk}} m_{jk} \left| F_{jk} \right|^2 \tag{1}$$

where I_0 is the incident beam intensity, Q is a combination of physical and geometrical parameters such as the speed of light in free space, the wavelength, the receiving slit width etc., V_k is the irradiated volume of the *k*th component in a specimen, μ is the linear absorption coefficient of the specimen, U_k is the unit-cell volume, $\sin \theta_{jk}$ is a parameter related to the geometry of scanning with the receiving slit, θ_{jk} is the Bragg angle, $(1 + \cos^2 2\theta_{jk})/2\sin 2\theta_{jk}$ is the Lorentz-polarization factor, m_{jk} is the multiplicity of the reflection, and F_{jk} is the structure factor. The weight W_k , corresponding to

^{*} Senior Adviser, Rigaku Corporation.

the volume V_k , is expressed as $W_k = V_k d_k$, where d_k is the material density calculated by $d_k = Z_k M_k / U_k$, where Z_k is the number of chemical formula units and M_k is the molecular weight. By replacing V_k and the geometrical factors in equation (1) by $V_k = W_k U_k / Z_k M_k$ and $G_{jk}^{-1} = (1 + \cos^2 2\theta_{jk})/2 \sin \theta_{jk} \sin 2\theta_{jk}$, respectively, equation (1) can be rewritten as

$$I_{jk} = I_0 \frac{QW_k}{\mu Z_k M_k U_k} G_{jk}^{-1} m_{jk} \left| F_{jk} \right|^2$$
(2)

By multiplying both terms of equation (2) by G_{jk} and summing them for all diffraction lines in the angular range $[2\theta_L, 2\theta_H]$ for respective components, we obtain

$$\sum_{j=1}^{N_{k}} I_{jk} G_{jk} = I_{0} \frac{Q}{\mu} \frac{W_{k}}{M_{k}} \frac{1}{Z_{k}} \left[\frac{1}{U_{k}} \sum_{j=1}^{N_{k}} m_{jk} \left| F_{jk} \right|^{2} \right]$$
(3)

where N_k is the number of diffraction lines, belonging to the *k*th component, in $[2\theta_L, 2\theta_H]$. The $[2\theta_L, 2\theta_H]$ range includes a diffraction line at the lowest angle and the proper number of diffraction lines for conducting QPA by the DD method⁽¹³⁾. It is important to note here that the quantity in parentheses of equation (3) is equivalent to the peak height of the Patterson function P(u,v,w) at the origin (0, 0, 0), and it holds that

$$\frac{1}{U_k} \sum_{j=1}^{N_k} m_{jk} \left| F_{jk} \right|^2 = P(0,0,0) \tag{4}$$

The peak height of the Patterson function can be approximated with its integrated value, just like the integrated intensity of a peak is approximated by the peak height (see Appendix), and then it holds

$$P(0,0,0) d \cong CZ_k \sum_{i=1}^{N_k^2} n_{ik}^2$$
(5)

where *C* is the proportionality constant, n_{ik} (*i*=1 to N_k^A) is the number of electrons belonging to the *i*th atom in the chemical formula, and N_k^A is the number of atoms in the chemical formula unit⁽¹³⁾. From equations (3) to (5), we obtain

$$\sum_{j=1}^{N_k} I_{jk} G_{jk} = I_0 \frac{Q}{\mu} \frac{W_k}{M_k} C \sum_{i=1}^{N_k^{\wedge}} n_{ik}^2$$
(6)

Hereupon the following two parameters S_k and a_k are defined for simplicity

$$S_k = \sum_{j=1}^{N_k} I_{jk} G_{jk} \tag{7}$$

$$a_k = M_k / \sum_{i=1}^{N_k^*} n_{ik}^2 \tag{8}$$

The weight fraction w_k is calculated by $w_k = W_k / \sum W_k (k' = 1 \text{ to } K)$, and from equations (6) to (8), we obtain the following equation.

$$w_k = a_k S_k / \sum_{k'=1}^{K} a_{k'} S_{k'} \tag{9}$$

The parameter a_k can be calculated only from the molecular weight and the numbers of electrons for individual atoms in the chemical formula unit. Therefore, the DD method makes it possible to conduct QPA if the chemical composition data are available. Equation (9) is called the Intensity-Composition formula (IC formula). Equations for calculating uncertainty in w_k [$\sigma(w_k$]] will be found in references 13 and 14.

3. Reliability of QPA by the IC formula

In this section, some examples of the application of the DD method are given⁽¹³⁾. Samples used for testing the reliability of QPA by the IC formula were prepared by mixing commercially available chemicals. Intensity data were collected with conventional type powder diffractometers based on Bragg–Brentano geometry [Rigaku Ultima IV and SmartLab equipped with a Cu target and a one-dimensional Si strip detector (D/teX Ultra or D/teX Ultra 250)]. Raw intensity data were processed using data analysis software PDXL, applying the automatic-mode for obtaining lists of integrated intensities for relevant phases. The accuracy in QPA was evaluated by the Root-Mean-Square Error (RMSE), defined by

$$RMSE = \left[\frac{1}{K}\sum_{k=1}^{K} \left(w_k - w_k^{\text{weighed}}\right)^2\right]^{1/2}$$
(10)

where w_k^{weighed} is the weighed values of chemicals in sample preparation.

3.1. Reproducibility of QPA in repeated scans

Reproducibility of QPA by the DD method was tested by using five intensity datasets collected by repeated scans. The sample used was a three-component mixture, containing TiO₂ (anatase), TiO₂ (rutile) and Si in weight ratios of 54.00:24.47:21.53 (wt.%), and it was repacked before each scan. Figure 1 shows variations of RMSE as a function of $2\theta_{\rm H}$ that was varied from 30° to $120^{\circ}/2\theta$. Horizontal dotted and broken lines represent the minimum and maximum RMSE for RIR and Rietveld QPA, respectively. Numbers represent the average values of RMSE for five repeated scans and numbers in parentheses are the standard deviations for the averages. RMSE's by the DD method generally decrease with increasing $2\theta_{\rm H}$, and they becomes less than 2% in $80^{\circ} \le 2\theta_{\rm H} \le 110^{\circ}$. A grand average in this angular range was 1.24%, and it is better than RMSE's of 1.61(15) and 1.82(18) by the Rietveld and RIR methods. The standard deviations for the five repeated scan was about 0.2%. This diagram indicates that the proper number of diffraction lines is necessary to conduct accurate QPA by the DD method, and in the present case using inorganic materials, intensity data up to the range of $80^{\circ} \le 2\theta_{\text{H}} \le 110^{\circ}$ should be included.

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Fig. 1. Variations of RMSE as a function of $2\theta_{\rm H}$ for five-time repeated scans. Sample is a mixture consisting of TiO₂ (anatase)+TiO₂ (rutile)+Si.

3.2. QPA of sample containing a strong scatter

Barium (Ba, atomic number 58) is a strong scatterer of X-rays, and it has a large influence on diffracted intensities. Figure 2 shows a QPA result of a threecomponent mixture consisting of BaSO₄ (barite), α -Al₂O₃ (corundum) and α -SiO₂ (α -quartz) in weight ratios of 50.27:38.13:11.60 wt.%. In the diagram, broken lines represent weighed values in sample preparation, and zigzag lines represent variations of w_k as a function of $2\theta_H$ for respective components. With increasing $2\theta_H$, which is linked with the number of integrated intensities in the S_k , from 30° to 120°/2 θ , weight fractions w_k closely approach weighed values in $80° \le 2\theta_H \le 110°$. Table 1 is a comparison of RMSE by the three method, showing that the DD method gave much lower RMSE than the other two methods.



Fig. 2. Variations of w_k as a function of $2\theta_H$ for a sample consisting BaSO₄ (barite)+ α -Al₂O₃ (corundum) + α -SiO₂ (α -quartz). Broken lines represent weighed values in sample preparation.

Table 1. Comparison of RMSE for weight fractions derived
by the three methods.

			Distuald	DID			
$2\theta_{\rm H}(^\circ)$	80	90	100	110	Average	Kletveld	KIK
RMSE	1.00	0.89	1.63	2.14	1.41	9.32	10.74

3.3. QPA of a sample containing preferentially oriented particles

Crystalline particles of calcite (CaCO₃), having strong cleavage planes, are apt to be preferentially oriented when they are packed into a flat specimen holder. A three-component mixture, consisting of CaCO₃, CaF₂ (fluorite) and TiO₂ (anatase) in weight ratios of 43.40:33.37:23.23 wt.%, was measured twice after being re-packed before each scan. RMSEs are compared in Table 2. RMSE's of ~3% by the DD method were higher than those by Rietveld QPA while they were much lower than those by the RIR method. The correction for preferred orientation in Rietveld QPA would be effective, while the averaging effect of systematic bias by summing up intensities in a wide 2θ -range would contribute to reduce the preferred orientation effect.

 Table 2.
 Comparison of RMSE's for weight fractions derived by the three methods.

	Saan	DD					Distuald	DID	
$2\theta_{\rm H}(^{\circ})$	Scan	80	90	100	110	Average	Kleivelu	NIK	
RMSE	1 st	2.02	4.30	3.05	2.02	2.85	1.47	12.32	
	2 nd	2.42	4.85	3.57	2.50	3.34	0.85	9.88	

3.4. QPA of a phase in minor amount

Accuracy in QPA of the minor phase simply depends on the accuracy in intensity measurement of individual phases. A three-component mixture (S_{FFT}) contains Fe_3O_4 (magnetite), Fe_2O_3 (hematite) and TiO_2 (anatase) in weight ratios of 62.87:35.00:2.13 wt.%, where TiO_2 is considered to be a minor phase. In the present case, seven peaks in a range of $20^{\circ} \le 2\theta \le 90^{\circ}$ were identified as those of TiO₂, and just two peaks among the seven were observed as resolved peaks. The remaining five were unresolved, overlapped with those of magnetite and/or hematite, and their integrated intensities must be partitioned among the relevant phases. The simplest way of partitioning is the equipartition (EqP), which allocates the total intensity of a peak evenly among the overlapping phases. A new method of intensity partitioning is the volumeproportional partition (VPP)⁽¹³⁾, which allocates the total intensity in proportion to irradiated volumes of the overlapped phases. It is an iterative process, starting from the intensities allocated by the EqP, deriving weight fractions as a first approximation, giving the irradiated volume by (weight fraction)/(the material density), and then allocating the intensity by the VPP.

Figure 3 shows variations of w_k as a function of $2\theta_H$ by using two sets of zigzag lines, one (ocher) represents QPA results obtained by applying the EqP and the other (brown) by the VPP. In this case, the EqP allocates excess intensities to the minor phase (TiO₂), resulting in overestimation, while the VPP gives reasonable results. Table 3 compares RMSEs in QPA by the three methods, together with another test result for the mixture (S_{ATC}) consisting of α -Al₂O₃+TiO₂ (Rutile)+CeO₂ in weight ratios of 95.23:3.72:1.05 wt.%. The lowest RMSE's were obtained by the DD method.



Fig. 3. Variation of w_k as a function of $2\theta_H$ for the sample of Fe₃O₄ (magnetite)+Fe₂O₃ (hematite)+TiO₂ (anatase). Broken lines represent weighed values in sample preparation.

 Table 3.
 Comparison of RMSEs for two mixtures containing phases in minor amounts.

	Sample	DD					Distant	DID
$2\theta_{\rm H}(^{\circ})$		80	90	100	110	Average	Kietvela	KIK
RMSE	S _{FFT}	1.16	0.39	0.33	0.55	0.61	0.84	1.33
(%)	SATC	0.38	0.35	0.27	0.39	0.35	0.59	0.77

3.5. QPA of a four-component mixture

Table 4 gives QPA results of a four-component mixture, consisting of CaF₂ (fluorite), TiO₂ (anatase), α -Al₂O₃ (corundum) and CaSO₄·2H₂O (gypsum) in weight ratios of 51.83:25.21:12.99:9.97 wt.%, intensity data of which were collected by two repeated scans. Gypsum, belonging to the monoclinic system, gives many crowded diffraction lines, and almost half of all peaks were overlapped with neighboring peaks of the remaining phases. QPA results derived by using integrated intensities, obtained by an individual profile fitting (IPF) technique gave high RMSE, while those using integrated intensities, obtained by the whole-powder-pattern decomposition (WPPD) method, gave RMSE of \sim 1wt.%, which is comparable to QPA results for materials with high crystallographic symmetry.

Table 4. Comparison of RMSEs for four-component mixture.

	Scan		DD	Distuald	DID	
		IPF(VPP)	IPP(EqP)	WPPD	Kietvelu	NIK
RMSE	1 st	20.88	14.29	1.04	4.92	31.73
(%)	2 nd	25.72	16.12	1.21	2.48	23.40

QPA of mixtures with indefinite chemical composition data

As indicated by equation (8), chemical composition data gives an exact value of the parameter a_k in the IC

formula. The a_k , however, exhibit interesting properties in QPA, and their utilization will expand applicability of the DD method⁽¹⁵⁾.

4.1. Values of *a_k* for compounds with similar chemical compositions

Table 5 gives values of a_k for a series of hydrated magnesium silicates (HMS) and hydro carbons (HC). These compounds consist of the same kinds of atoms but they differ in the numbers of atoms. Both M_k and $\sum n_{ki}^2$ increase when the total number of atoms increases. However, the value of a_k is almost constant. The standard deviations for the averages of a_k (a^{av}) are just 0.02% and 0.32% for HMS and HC, respectively. For example, we prepared a mixture consisting of four compounds of HMS in Table 5, weighing evenly (25.0 wt.% for each), and conducted QPA by the DD method using the a^{av} . In this case, the estimated error arising from the use of a^{av} instead of individual a_k values is just $\sigma(w_k)/w_k = 0.00018$, and it can be ignored in practice: the error in w_k caused by the error in a_k can be estimated by using equations (11) and (12) in the report⁽¹⁵⁾.</sup>

Ultimate cases of the compounds with similar chemical compositions are polymorphs and polytypes, having the same chemical composition but with different crystal structures and physical properties in general. In this case, values of a_k are all equivalent, and the parameter a_k can be cancelled out from the IC formula, giving a form

$$w_{k} = S_{k} / \sum_{k'=1}^{K} S_{k'}$$
(11)

In this case, even chemical composition data are not required, and only observed intensity data will give accurate QPA results. Equation (11) can also be applied to QPA of compounds with similar chemical compositions if we can ignore $\sigma(w_k)/w_k$ as discussed above.

Table 5. Values of a_k for a series of hydrated magnesiumsilicates (HMS) and hydro carbons (HC).

	Chemical composition	M_k	$\sum n_{ki}^2$	a_k
HMS	Mg ₃ (SiO ₄)(OH) ₂	199.034	1046	0.19028
	Mg ₅ (SiO ₄) ₂ (OH) ₂	339.742	1786	0.19023
	Mg ₇ (SiO ₄) ₃ (OH) ₂	480.450	2526	0.19020
	$Mg_9(SiO_4)_4(OH)_2$	621.157	3266	0.19019
	Average a_k			0.19022 (4)
HC	C10H8	128.175	368	0.3483
	$C_{14}H_{10}$	178.235	514	0.3468
	$C_{18}H_{12}$	228.295	660	0.3459
	$C_{22}H_{14}$	278.356	806	0.3454
	Average a_k			0.3466 (11)

4.2. QPA of natural products

Rock-forming minerals contain various trace

elements, such as Li, Ti, Cr, Mn, Ni, Ca, Cs, Ba etc., and include substitutional replacements of metal ions like $Si^{4+} \leftrightarrow Al^{3+}$, $Fe^{2+} \leftrightarrow Mg^{2+}$ etc. over different crystallographic sites. Their chemical compositions are, in general, much more complicated than their ideal chemical formulae. Industrial products and byproducts like cements and slugs also have complex chemical formulas. The parameter a_k depends simply on the chemical composition, and is not concerned with the distribution of metals/ions over specific crystallographic sites. Moreover, the replacement of Fe with Cr, Mn, Co or Ni, for example, will not change the value of a_k in an appreciable amount and, as a result, will not affect results of QPA by the DD method beyond the level of statistical errors.

Table 6 gives average values of $a_k (a^{av})$ and their standard deviations $[\sigma(a^{av})]$, together with maximum deviations from the a^{av} (Δa_k^{\min} and Δa_k^{\max}), for some representative rock-forming minerals. These values of a^{av} are the averages of individual a_k values, which were calculated using chemical composition data, including various trace elements, reported for individual rockforming minerals collected from all over the world^{(17), (18)}, and the values of N at the end of Table 6 represent the numbers of data used for calculating the a^{av} .

Weathered granites are used as raw materials in the ceramics industry, and their main constituent rock-forming minerals are α -quartz, orthoclase, albite and biotite in weight ratios, reported as a representative case, of 48:37:11:4⁽¹⁹⁾. Table 7 gives a result of simulated QPA of weathered granite. Weight fractions w_k in the fourth column were obtained, when S_k in the 2nd column were given and a_k in the 3rd column were used to derive them. In this simulation, the a^{av} in Table 6 were used instead of a_k for a particular locality. In reality, a_k will

vary from one geographical locality to another. Then a_k were varied by $a^{av} \pm \sigma (a^{av})$, and variations of w_k , associated with varying $\pm \sigma (a^{av})$, were expressed as Δw_k . Average values of $|\Delta w|$ for respective minerals were 0.33, 0.51, 0.10 and 0.16% (the grand average=0.27%), and they are in a good agreement with 0.37, 0.48, 0.11 and 0.15% (the grand average=0.28%), which were estimated by using equations (11) and (12) in the report⁽¹⁵⁾. Uncertainty in w_k associated with the uncertainty in a_k is expected to be much decreased if chemical analysis data, stored in the databases for individual localities, are used.

4.3. **QPA of an unknown phase**

The DD method can quantify the target mixture if integrated intensities are measured for individual phases and chemical composition data are available. When one phase in the mixture is unknown with respect to the chemical composition, it can be quantified if its chemical composition is estimated from the chemical composition data of other phases or those of starting materials from which the target mixture sample was synthesized. When the chemical composition of an unknown phase could not be inferred, the a_k for the unknown phase $(a_{\rm UK})$ can be calculated by⁽¹⁵⁾

$$a_{\rm UK} = \frac{1}{S_{\rm UK}} \left(a_{\rm B} \sum_{k'=1}^{K} S_{k'} - \sum_{k'=1}^{K-1} a_{k'} S_{k'} \right)$$
(12)

where S_{UK} is the S_k for the unknown phase and a_{B} is the a_k for the batch chemical composition. Details of the procedure will be found in reference (15).

5. Summary

1) Weight fractions (w_k) of individual crystalline

Mineral/group	Ideal chemical formula	a ^{av}	$\sigma(a^{\rm av})$	Δa_k^{\min}	Δa_k^{\max}	Ν
Olivine	(Mg,Fe) ₂ SiO ₄	0.1554	0.0257	-0.0420	0.0341	21
Orthopyroxene	(Mg,Fe)SiO ₃	0.1599	0.0143	-0.0251	0.0278	19
Anthophyllite	(Mg,Fe) ₇ Si ₈ O ₂₂ (OH) ₂	0.1696	0.0090	-0.0145	0.0105	11
Muscovite	KAl ₂ Si ₃ AlO ₁₀ (OH) ₂	0.1709	0.0091	-0.0318	0.0074	15
Biotite (igneous)	K(Fe,Mg) ₃ Si ₃ AlO ₁₀ (OH) ₂	0.1461	0.0055	-0.0100	0.0083	16
Orthoclase	KSi ₃ AlO ₈	0.1756	0.0036	-0.0070	0.0064	16
Albite	NaSi ₃ AlO ₈	0.1868	0.0013	-0.0020	0.0017	14

Table 6. Ideal chemical formulae, a^{av} values and related parameters for some representative rock-forming minerals.

Table 7. Result of simulated QPA for weathered granite.

Component	C		$100 \times w_k$	$100 \times \Delta w_k(\%)$						
	S_k	a_k	(%)	+	-+-	+	-++	+-+	++-	
Quartz	4657.0	0.1854	48.0	-0.26	0.41	0.33	0.26	-0.40	-0.33	
Orthoclase	3790.5	0.1756	37.0	0.56	-0.46	-0.51	-0.57	0.45	0.50	
Albite	1059.7	0.1868	11.0	-0.13	0.17	0.00	0.13	-0.17	-0.00	
Biotite	492.8	0.1461	4.0	-0.17	-0.12	0.18	0.17	0.12	-0.18	

phases can be derived from sets of observed integrated intensities and chemical composition data for the respective phases. QPA can be conducted irrespective of whether the crystal structures of individual phases are known or unknown.

- 2) Since integrated intensities measured in a wide 2θ range are used, the accuracy in QPA by the DD method is comparable to that by Rietveld QPA. Even when the intensity data are biased, because of preferred orientation for example, systematic error can be reduced compared to the technique using single peak intensities.
- Even when the chemical compositions are indefinite, derived weight fractions will not largely be influenced.
- 4) An unknown phase can be quantified if its chemical composition is estimated.
- 5) Whole-powder-pattern decomposition techniques are a powerful tool to obtain accurate integrated intensities, and they will contribute to extend target materials to be quantified by the DD method.

More sophisticated application of the DD method is to be reported⁽²¹⁾.

Appendix: The Patterson function

What we observe in crystal structure analysis using the X-ray diffraction method is the electrons surrounding the nuclei. The electron density distribution function $\rho(x, y, z)$, which represents the electron density distribution in a crystal, is expressed by using Fourier series of the form,

$$\rho(x, y, z) = \frac{1}{U} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} F(hkl) \exp\left[-2\pi i (hx + ky + lz)\right] \quad (13)$$

where *x*, *y*, *z* are fractional coordinates of atoms in the unit cell. The Patterson function is defined as a self-convolution of the $\rho(x, y, z)$, and it is given by⁽²⁰⁾.

$$P(u,v,w) = U \int_0^1 \int_0^1 \int_0^1 \rho(x,y,z) \,\rho(x+u,y+v,z+w) \, dx \, dy \, dz \quad (14)$$

Substituting equation (13) into equation (14), we obtain

$$P(u,v,w) = \frac{1}{U} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \left| F(hkl) \right|^2 \cos \left[2\pi (hu + kv + lw) \right]$$
(15)

The Patterson function at the origin, u, v, w=0, 0, 0, has a form

$$P(0,0,0) = \frac{1}{U} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \left| F(hkl) \right|^2$$
(16)

The Patterson function is a periodic function having the same periodicities as those of the unit-cell of the original crystal. Since it is the self-convolution of the $\rho(x, y, z)$, it has peaks at the positions corresponding to the interatomic vectors from the origin of Patterson space. For example, if two atoms A and B are present in the unit-cell, there will be four interatomic vectors of \overline{AA} , \overline{AB} , \overline{BA} and \overline{BB} . There is a vector \overline{AB} from the origin of the Patterson space, and \overline{BA} on the opposite direction from the origin. Furthermore, two peaks corresponding to \overline{AA} and \overline{BB} are superposed at the origin.

If we integrate $\rho(x, y, z)$ from the center of an atom to the boundary with neighboring atoms, the integrated value will be identical to the number of electrons belonging to the atom. The problem will be simplified by thinking of a one-dimensional lattice and the normalized Gaussian function G(x) to represent the $\rho(x) = nG(x)$ for an atom, where *n* is the number of electrons of the atom. If we integrate $\rho(x)$, $\int \rho(x) dx = n$. The Patterson function is defined by P(u) $=\int \rho(x)\rho(x+u)dx$, and the convolution of the Gaussian function with the another Gaussian function is a Gaussian function. Therefore, $\int n_A G(x) \times n_B G'(x+u) dx$ $=n_A n_B G''(u)$. If we integrate the peak in the Patterson space around the position of the interatomic vector \overline{AB} , it will be $\int n_A n_B G''(u) du = n_A n_B$. If we integrate the Patterson function having two superimposed peaks of $n_A n_A G''$ and $n_B n_B G''$ at the origin, its integral value will be identical to $n_{\rm A}^2 + n_{\rm B}^2$.

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