NEW APPROACH TO ELIMINATE THE INSTRUMENTAL ABERRATIONS FROM POWDER X-RAY DIFFRACTION DATA BASED ON A FOURIER METHOD

TAKASHI IDA

Ceramics Research Laboratory, Nagoya Institute of Technology, Asahigaoka 10-6-29, Tajimi, Gifu 507-0071, Japan

A new approach to eliminate the effects of spectroscopic properties of the source X-ray and instrumental aberrations of powder diffractometers is presented. The method is based on the scale transformation, interpolation of data and fast Fourier transformation. The entire diffraction data over wide range of diffraction angles can be simultaneously deconvoluted on the appropriate scale of abscissa. Analytical expressions of the instrumental function for a Bragg–Brentano powder diffractometer are fully utilized to evaluate the deconvolution. The errors in the deconvoluted data propagated from the statistical uncertainty in the source data are also evaluated by the Fourier method. An efficient numerical evaluation of deconvolution is achieved by applying fast Fourier transform technique.

1. Introduction

The experimental powder diffraction peak profiles are affected not only by the crystallographic structures or microstructures of powder or polycrystalline specimens, but also by the spectroscopic properties of the X-ray source and optical aberrations of the diffractometers. The effects of those aberrations are approximately represented by the convolution with the instrumental function. When the “experimental profiles”, “intrinsic profiles” and “instrumental functions” are represented by the functions \( p(x) \), \( f(x) \) and \( w(x) \), respectively, the convolution relation is expressed as

\[
\int_{-\infty}^{\infty} p(x-y)w(y)dy
\]

(1)

The intrinsic profile \( f(x) \) can be derived from the experimental profile \( p(x) \) and instrumental function \( w(x) \) by applying the following deconvolution procedure based on a Fourier method,

\[
P(k) = \int_{-\infty}^{\infty} p(x) \exp(2\pi ikx)dx
\]

(2)

\[
W(k) = \int_{-\infty}^{\infty} w(x) \exp(2\pi ikx)dx
\]

(3)

\[
f(x) = \frac{1}{W(k)} \int_{-\infty}^{\infty} P(k) \exp(-2\pi ikx)dk
\]

(4)

Stokes has shown that the experimental diffraction peak profile of a well-annealed specimen can be used as the substitution for the instrumental function. The method of Stokes has been applied for analysis of diffraction peak profile during the past five decades [2, 3], even though the validity of the method is restricted only for a narrow angular range of the diffraction data, in principle.

In this paper, a new Fourier-based deconvolution method for eliminating instrumental aberrations from experimental powder diffraction data is proposed. The method is more advantageous than the conventional method of Stokes at the following points: (i) measurement of standard material is not needed, because the analytical expressions of the instrumental aberrations are properly used as the instrumental functions; (ii) the whole powder diffraction data over wide range of diffraction angles are simultaneously processed within short computing time; (iii) the estimation of error propagation through the deconvolution process is possible, which enables application of weighted least squares analysis to the deconvoluted data.

2. Theoretical Framework

It is considered that the total instrumental function of a powder diffractometer should be a multiple convolution of various instrumental aberrations caused by different origins [4]. The dependence of the profile of the instrumental function on the diffraction angle is consequently quite complicated. However, the angu-
lar dependence of each component aberration function is not formidable complicated, and most of the aberration functions show only change in width keeping the similar shape of the profile [5]. In such a case, the whole diffraction data can be considered as a convolution with a common instrumental function, when we apply an appropriate scale transformation for the abscissa [6].

Figure 1(a) shows a part of the powder diffraction pattern of LaB$_6$ standard powder sample (NIST SRM660) measured with a laboratory diffractometer. Since the CuK$_\alpha$ radiation is used as the X-ray source, each reflection exhibits a doublet of K$_\alpha_1$ and K$_\alpha_2$ peaks. The separation of the K$_\alpha_1$ and K$_\alpha_2$ peaks is larger in the higher angle range, while it becomes smaller in the lower angle range. It indicates that the convolution relation is only locally valid, and the whole diffraction data cannot be treated as a convolution with a unique instrumental function. However, one can imagine that the diffractogram with evenly separated doublets may be created, if the abscissa scale in the lower angle range are stretched and/or the scale in the higher angle range is compressed. When the same diffraction data are plotted on the abscissa scale of ln(sin $\theta$) instead of $2\theta$, the diffractogram certainly exhibits evenly separated doublets as shown in Fig. 1(b), which means that the whole pattern can be treated as a convolution with the common instrumental function for the diagram shown in Fig. 1(b).

2.1. Scale Transformation

We assume that the dependence of the instrumental aberration function on the diffraction angle keeps similar shape and is completely described only by the angular dependence of a width parameter $\gamma(2\theta)$. Then the instrumental function $\omega(\Delta 2\theta; 2\theta)$ can be represented by using a function with single argument $w(x)$, as

$$\omega(\Delta 2\theta; 2\theta) = w\left(\frac{\Delta 2\theta}{\beta \gamma(2\theta)}\right)$$  \hspace{1cm} (5)

where $\beta$ is a constant parameter independent of $2\theta$. When the primitive function of the reciprocal of $\gamma(2\theta)$ is represented by $G(2\theta)$, that is,

$$G(2\theta) = \int \frac{d(2\theta)}{\gamma(2\theta)}$$  \hspace{1cm} (6)

the new scale defined by $\chi = G(2\theta)$ satisfies the following relation,

$$\frac{\Delta \chi}{\Delta 2\theta} = \frac{1}{\gamma(2\theta)}$$  \hspace{1cm} (7)

which means that the angle-dependent width on the $2\theta$-scale, $\beta \gamma(2\theta)$, corresponds to the constant width $\beta$ on the $\chi$-scale. Therefore, the peak profile on the $\chi$-scale can be represented as the convolution with a unique instrumental function $w(\chi/\beta)$, which means that the instrumental function can be removed from the entire data by a standard Fourier deconvolution method on the $\chi$-scale.
The raw experimental diffraction data are assumed to be given by the sets of diffraction angles \(2\theta_m\) and the error data \(\Delta S_m\) \((m=0, \ldots, M-1)\). The scale-transformed data sets for abscissa \(\{x_n\}\) and ordinate \(\{y_n\}\) and error \(\{\eta_n\}\) are calculated by

\[
\begin{align*}
\chi_m &\leftarrow \gamma(2\theta_m) \quad (8) \\
\eta_m &\leftarrow \gamma(2\theta_m)S_m \quad \eta_m = \frac{\gamma(2\theta_m)S_m}{C(2\theta_m)} \quad (9) \\
\Delta \eta_m &\leftarrow \gamma(2\theta_m)S_m \quad \Delta \eta_m = \frac{\gamma(2\theta_m)S_m}{C(2\theta_m)} \quad (10)
\end{align*}
\]

where the function \(C(2\theta)\) represents the intensity correction for powder diffractometry given by

\[
C(2\theta) = \frac{1 + A \cos^2 2\theta}{(1 + A)\sin \theta \sin 2\theta} \quad (11)
\]

and

\[
A = \cos 2\theta_m \quad (12)
\]

with a monochromator of the diffraction angle \(2\theta_m\) or \(A=1\) without a monochromator.

### 2.2. Interpolation

The scale-transformed data points of abscissa \(\{x_n\}\) \((m=0, \ldots, M-1)\) obtained by the procedure described in the preceding section are not evenly spaced. Application of the fast Fourier transform (FFT) algorithm for the calculation of convolution is enabled by creating evenly spaced data by interpolation. The cubic spline interpolation algorithm is conveniently applied to create evenly spaced data sets of abscissa \(\{x_n\}\) and ordinate \(\{y_n\}\) \((n=0, \ldots, N-1)\), from the sets of \(\{x_n\}\) and \(\{\eta_n\}\) \((m=0, \ldots, M-1)\). The number of the interpolated data \(N\) should be less than the total number of data points \(N\) (an integer power of 2) used for the FFT calculation to avoid boundary effect in the discrete Fourier transform by filling \((N-N')\) data with zero. The interval of the \(\{x_n\}\)-data should be finer than the minimum interval in the \(\{x_m\}\)-data.

In order to keep the statistical properties of the data unchanged through the interpolation process, the error data \(\{\Delta \eta_n\}\) are further modified to \(\{\Delta \eta'_n\}\) by the following equation,

\[
\Delta \eta'_n = \frac{\Delta x}{\Delta x_m} \Delta \eta_m \quad (13)
\]

before the interpolation process, where \(\Delta x_m\) and \(\Delta x\) are the intervals of the source and interpolated data. Then, the error data \(\{\sigma_n\}\) for evenly sampled ordinate \(\{y_n\}\) are similarly created from \(\{\Delta \eta'_n\}\) by a cubic spline interpolation.

### 2.3. Deconvolution of Instrumental Function

The Fourier transform \(W(\xi)\) of the instrumental function \(w(x)\) is defined by

\[
W(\xi) = \int_{-\infty}^{\infty} w(x) \exp(2\pi i \xi x) dx \quad (14)
\]

Assuming that the instrumental function is represented by a discrete formula \(\{w_n\} (n=0, \ldots, N)\), the discrete Fourier transform is given by

\[
W_k = \sum_{n=0}^{N-1} w_n \exp\left(\frac{2\pi i kn}{N}\right) \quad (k = -N/2, \ldots, N/2) \quad (15)
\]

where the periodicity of \(W_k = W_{k+N} \) is implicitly assumed. It is less ambiguous for the discrete formula \(\{w_n\}\) to be treated as the inverse Fourier transform of the discrete Fourier coefficient \(\{W_k\}\), when the analytical formula \(W(\xi)\) for the Fourier transform of the instrumental function is available.

The discrete Fourier coefficient \(\{W_k\}\) is connected with the analytical form of the Fourier transform \(W(\xi)\) by the following relation:

\[
W_k = W\left(\frac{k}{N\Delta x}\right) \quad (k = -N/2, \ldots, N/2) \quad (16)
\]

where \(\Delta x\) is the sampling interval of the data. The discrete formula of the instrumental function \(\{w_n\}\) is given by

\[
w_n = \frac{1}{N} \sum_{k=-N/2}^{N/2-1} W_k \exp\left(-\frac{2\pi i kn}{N}\right) \quad (17)
\]

It should be noted that the following discrete convolution relation is satisfied,

\[
y_n = \sum_{m=0}^{N-1} z_{n-m} w_m \quad (18)
\]

for the source data \(\{y_n\}\), deconvolution \(\{z_n\}\) and instrumental function \(\{w_n\}\).

The deconvoluted intensity data \(\{z_n\}\) are calculated by the inverse Fourier transform:

\[
z_n = \frac{1}{N} \sum_{k=-N/2}^{N/2-1} Y_k \exp\left(-\frac{2\pi i kn}{N}\right) \quad (19)
\]

where \(\{Y_k\}\) is the discrete Fourier transform of \(\{y_n\}\), which is given by
2.4. Error Propagation through Deconvolution

Provided that \( \{y_n\} \) is evenly sampled data, the FFT algorithm can be applied for all the numerical calculations of Fourier and inverse Fourier transforms.

### 2.4.1 Error Propagation through Deconvolution

In this section, the propagation of the error \( \{e_n\} \) attached to the source data \( \{y_n\} \) into the deconvolution \( \{z_n\} \) is discussed.

When we define the "inverse instrumental function" \( \{w_n^{(-1)}\} \) by the following equation,

\[
w_n^{(-1)} = \frac{1}{N} \sum_{k=-N/2}^{N/2-1} \frac{1}{W_k} \exp \left(-\frac{2\pi ikn}{N}\right) \tag{21}\]

the elements of the covariance (error) matrix for the deconvoluted data \( \{z_n\} \) are given by

\[
S_{mn} = \sum_{k=0}^{N-1} \sigma_k^2 w_{m-k} w_{n-k} \tag{22}\]

and the elements of the weight matrix, which is identical to the inverse of the covariance matrix, are given by

\[
T_{mn} = \sum_{k=0}^{N-1} \sigma_k^{-2} w_{k-m} w_{k-n} \tag{23}\]

When we neglect the off-diagonal elements of the matrices, two different indicators, \( \{\delta_n\} \) and \( \{e_n\} \), for the errors of the deconvoluted data \( \{z_n\} \) are derived by the following equations,

\[
\delta_n^2 = T_m = \sum_{i=0}^{N-1} \sigma_i^{-2} w_i^{(-1)} \tag{24}\]

\[
e_n^2 = S_{nn} = \sum_{i=0}^{N-1} \sigma_i^2 [w_i^{(-1)}]^2 \tag{25}\]

that is, \( \{\delta_n^2\} \) is the correlation between \( \{\sigma_n^2\} \) and \( \{w_i^2\} \), and \( \{e_n^2\} \) is the convolution of \( \{\sigma_n^2\} \) with \( \{[w_i^{(-1)}]^2\} \). Both of the indicators can be easily evaluated by the FFT method.

### 3. Application to a Bragg–Brentano Diffractometer

#### 3.1. Instrumental Functions

The main instrumental aberrations of most commonly used Bragg–Brentano type diffractometers are: (i) spectroscopic distribution of the source X-ray, (ii) axial divergence aberration, (iii) flat-specimen aberration and (iv) aberration caused by sample transparency. The instrumental functions, appropriate scale transforms and the analytical formulas of the Fourier transforms for each aberration are discussed in this section.

#### 3.1.1 Spectroscopic Properties of CuKα Radiation

The experimental peak profiles are affected by the spectroscopic properties of the source X-ray, most significantly in the high diffraction angle range. The CuKα radiation, which is frequently used as the X-ray source for laboratory diffractometers, exhibits double peaks corresponding to Kα1 and Kα2 radiations. Numerous methods have been proposed to eliminate the unwanted Kα2 lines [7–12], but it seems that the new method described in this paper is more advantageous for the simplicity in both theoretical and practical aspects.

The spectroscopic intensity profile is approximated by the weighted sum of two Lorentzian functions,

\[
f_2(\lambda) = (1 - \rho) f_1(\lambda - \lambda_1; \Delta \lambda_1/2) + \rho f_3(\lambda - \lambda_2; \Delta \lambda_2/2) \tag{26}\]

where \( \lambda_1 \) and \( \lambda_2 \) are the peak positions, \( \Delta \lambda_1 \) and \( \Delta \lambda_2 \) are the full widths at half maximum of the Kα1 and Kα2 radiations, respectively, and \( f_1(x; \omega) \) is the Lorentzian function defined by

\[
f_1(x; \omega) = \frac{1}{\omega^2} \left[ 1 + \left( \frac{x}{\omega} \right)^2 \right]^{-1} \tag{27}\]

The effect of the spectroscopic profile on the diffraction peak profile is approximately given by

\[
\omega(\Delta 2\theta) = (1 - \rho) f_1(\Delta 2\theta; \omega_1) + \rho f_3(\Delta 2\theta - 2\theta; \omega_2) \tag{28}\]

\[
2\theta_2 = 2 \arcsin \left( \frac{\lambda_2}{\omega} \sin \frac{2\theta_1}{2} \right) \tag{29}\]

\[
w_j = \frac{\Delta \lambda_j \tan \theta_1}{\lambda_j} \quad (j = 1, 2) \tag{30}\]

where \( 2\theta_1 \) is the Kα1 peak position.

For the purpose of eliminating the Kα2 sub-peak, the following formula can be applied as the instrumental function,

\[
\omega_{\alpha 2}(\Delta 2\theta) = (1 - \rho) \delta(\Delta 2\theta) + \rho f_3(\Delta 2\theta - 2\theta + 2\theta_1; \omega_2 - \omega_1) \tag{31}\]

which is connected with the function \( \omega_X(\Delta 2\theta) \).
by the following convolution relation,
\[ \omega_x(\Delta 2 \theta) = \int \omega_x^s(\Delta 2 \theta; w_1) * \omega_{x2}(\Delta 2 \theta) \]
(32)
The separation of the K\alpha_1 and K\alpha_2 peaks is approximated by
\[ 2\theta_2 - 2\theta_1 \sim \frac{(\lambda_2 - \lambda_1) \gamma_1}{\lambda_1} \]
(33)
and the slight broadening of the K\alpha_2 peak is approximated by
\[ \omega_2 - \omega_1 \sim \frac{(\Delta \lambda_2 - \Delta \lambda_1) \gamma_1}{2 \lambda_1} \]
(34)
where \( \gamma_1 \) is an angle-dependent parameter defined by
\[ \gamma_1 = 2 \tan \theta \]
(35)
When we define the following two angle-independent parameters,
\[ \beta = \frac{\lambda_2 - \lambda_1}{\lambda_1} \]
(36)
\[ \Delta \beta = \frac{\Delta \lambda_2 - \Delta \lambda_1}{2 \lambda_1} \]
(37)
the function \( \omega_{x2}(\Delta 2 \theta) \) is rewritten as
\[ \omega_{x2}(\Delta 2 \theta) = (1 - \rho) \delta(\Delta 2 \theta) + \rho f(\Delta 2 \theta - \beta_{x2} \gamma_1; \Delta \beta_{x2} \gamma_1) \]
(38)
Since the width of the peak profile of the \( \omega_{x2}(\Delta 2 \theta) \) function is proportional to \( \gamma_1 \), the angle-independent formula of the instrumental function can be obtained by the following scale transformation from \( \theta_2 \) to \( \chi_1 \),
\[ \chi_1 = G_1(2 \theta) = \int \frac{d(2 \theta)}{\gamma_1} = \ln(\sin \theta) \]
(39)
The instrumental function on the \( \chi \)-scale is given by
\[ \omega_{x2}(\chi_1) = (1 - \rho) \delta(\chi_1) + \rho f(\chi_1 - \beta_{x2}; \Delta \beta_{x2}) \]
(40)
and the analytical Fourier transform of the function \( \omega_{x2}(\chi_1) \) is given by
\[ W_{x2}(\xi) = \int \omega_{x2}(\chi_1) \exp(2 \pi i \xi \chi_1) d\chi_1 = 1 - \rho + \rho \exp[2 \pi i (\xi \beta_{x2} - | \xi | \Delta \beta_{x2})] \]
(41)
The following values of the constants \( \rho, \lambda_1, \lambda_2, \Delta \lambda_1, \) and \( \Delta \lambda_2 \) for the CuK\alpha radiation can be used,
\[ \rho = 1/3, \lambda_1 = 0.15405981 \text{ nm}, \lambda_2 = 0.154443 \text{ nm}, \Delta \lambda_1 = 0.000058 \text{ nm}, \Delta \lambda_2 = 0.000077 \text{ nm} \]

### 3.1.2. Axial Divergence Aberration

The instrumental function for the axial divergence aberration is given by
\[ \omega_A(\Delta 2 \theta) = \frac{1}{2 \pi \beta_A} \exp \left[ \frac{1}{\gamma_2} \left( \frac{1}{\gamma_1} \right) \right. \]
\[ \left. \frac{\Delta 2 \theta}{\Delta \theta} \right] \]
(42)
where \( \gamma_1 = 2 \tan \theta \) and \( \gamma_2 = 2 \tan \theta \) are the angle-dependent parameters, \( \phi_A \) is the full width at half-maximum of the intensity profile along the axial direction, and \( K_q(x) \) is the modified Bessel function of the second kind [13]. The function \( \omega_A(\Delta 2 \theta) \) is exactly equivalent to the convolution of the following two functions:
\[ \omega_A(\Delta 2 \theta) = \begin{cases} 1 & \text{for } \Delta 2 \theta > 0 \\ \frac{1}{\pi^{1/2} \beta_A \gamma_1} \beta_A \gamma_1^{1/2} \exp \left( -\frac{\Delta 2 \theta}{\beta_A \gamma_1} \right) & \text{elsewhere} \end{cases} \]
(44)
and
\[ \omega_A(\Delta 2 \theta) = \begin{cases} 1 & \text{for } \Delta 2 \theta < 0 \\ \frac{1}{\pi^{1/2} \beta_A \gamma_2} \beta_A \gamma_2^{1/2} \exp \left( -\frac{\Delta 2 \theta}{\beta_A \gamma_2} \right) & \text{elsewhere} \end{cases} \]
(45)
that is,
\[ \omega_A(\Delta 2 \theta) = \omega_+ \times \omega_- \]
(46)
The upper-angle component of the axial-divergence aberration function, \( \omega_A(\Delta 2 \theta) \), can be transformed to the angle-independent formula by applying the scale transform:
\[ \chi_1 = G_1(2 \theta) = \ln(\sin \theta) \]
(47)
which gives
The analytical Fourier transform of the function \( w_A(\chi_1) \) is given by

\[
W_A(\xi) = \int w_A(\chi_1) \exp(2\pi i \xi \chi_1) d\chi_1 = \sqrt{1 + 4\pi^2 \xi^2 \beta_A^2 + 1 + i\sqrt{1 + 4\pi^2 \xi^2 \beta_A^2 - 1}} \]

\[
= \frac{1}{\sqrt{2(1 + 4\pi^2 \xi^2 \beta_A^2)}}
\]

The lower-angle component of the axial-divergence aberration function, \( w_A(\Delta \theta) \), can be transformed to the angle-independent formula by applying another scale transform:

\[
\chi_2 = G_2(\Delta \theta) = \frac{d(\Delta \theta)}{\gamma_2} = -\ln(\cos \theta)
\]

which gives

\[
w_A(\chi_2) = \begin{cases} \frac{1}{\beta_A} \sqrt{1 + 4\pi^2 \xi^2 \beta_A^2 + 1 + i\sqrt{1 + 4\pi^2 \xi^2 \beta_A^2 - 1}} & \text{for } \chi_2 < 0 \\
0 & \text{elsewhere} \end{cases}
\]

The Fourier transform of the function \( W_A(\chi_2) \) is given by

\[
W_A(\xi) = \int w_A(\chi_2) \exp(2\pi i \xi \chi_2) d\chi_2
\]

\[
= \frac{1}{\sqrt{2(1 + 4\pi^2 \xi^2 \beta_A^2)}}
\]

In summary, the axial divergence aberration can be eliminated from the entire diffraction pattern by two-step deconvolutions of \( w_A(\Delta \theta) \) on the \( \ln(\sin \theta) \)-scale and \( w_A(\Delta \theta) \) on the \( -\ln(\cos \theta) \)-scale.

3.1.3. Flat-specimen Aberration

The flat-specimen aberration function on the \( 2\theta \) scale is given by

\[
\omega_F(\Delta \theta) = \begin{cases} \frac{1}{2\beta_F \gamma_2} \sqrt{1 + 4\pi^2 \xi^2 \beta_F^2 + 1 + i\sqrt{1 + 4\pi^2 \xi^2 \beta_F^2 - 1}} & \text{for } -\beta_F \gamma_2 < \Delta \theta < 0 \\
0 & \text{elsewhere} \end{cases}
\]

\[
\beta_F = \frac{\phi^*}{4}
\]

where \( \gamma_2 = 2/\tan \theta \) is the angle-dependent parameter, and \( \phi^* \) is the equatorial divergence angle, which is identical to the fixed open angle of the divergence and scattering slits [4, 14].

The angle-independent formula of the flat-specimen aberration function is available on the scale \( \chi_2 = -\ln(\cos \theta) \), which is given by

\[
w_F(\chi_2) = \begin{cases} \frac{1}{2\beta_F} \sqrt{1 + 4\pi^2 \xi^2 \beta_F^2 + 1 + i\sqrt{1 + 4\pi^2 \xi^2 \beta_F^2 - 1}} & \text{for } -\beta_F < \chi_2 < 0 \\
0 & \text{elsewhere} \end{cases}
\]

and the Fourier transform of the function \( w_F(\chi_2) \) is given by

\[
W_F(\xi) = \int w_F(\chi_2) \exp(2\pi i \xi \chi_2) d\chi_2
\]

\[
= \frac{C(2\sqrt{\xi^2 \beta_F}) - iS(2\sqrt{\xi^2 \beta_F})}{2\sqrt{\xi^2 \beta_F}}
\]

where \( C(x) \) and \( S(x) \) are the Fresnel functions defined by

\[
C(x) = \int_0^x \cos \frac{\pi t^2}{2} dt
\]

\[
S(x) = \int_0^x \sin \frac{\pi t^2}{2} dt
\]

3.1.4. Effect of Sample Transperancy

When the thickness of the specimen is sufficiently greater than the penetration depth of the source X-ray, the instrumental function for the effect of sample transparency on the \( 2\theta \)-scale is given by

\[
\omega_F(\Delta \theta) = \begin{cases} \frac{1}{2\beta_F \gamma_3} \sqrt{1 + 4\pi^2 \xi^2 \beta_F^2 + 1 + i\sqrt{1 + 4\pi^2 \xi^2 \beta_F^2 - 1}} & \text{for } \Delta \theta < 0 \\
0 & \text{elsewhere} \end{cases}
\]

\[
\beta_F = \frac{1}{2\mu R}
\]

where \( \gamma_3 = \sin 2\theta \) is the angle-dependent parameter, \( \mu \) the linear absorption coefficient of the specimen, and \( R \) the goniometer radius [5]. The sample-transparency aberration function,
$w_T(TD^2q)$, can be transformed to the angle-independent formula by applying the third type of scale transform:

$$X_3 = G_3(2\theta) = \frac{d(2\theta)}{\gamma_3} = \ln(\tan \theta) \quad (61)$$

The instrumental function independent of $2\theta$ is then given by

$$w_1(X_3) = \begin{cases} 1 \exp\left(\frac{X_3}{\beta_T}\right) & \text{for } X_3 < 0 \\ 0 & \text{elsewhere} \end{cases} \quad (62)$$

The Fourier transform of the function $w_1(X_3)$ is given by

$$W_1(\xi) = \int w_1(X_3) \exp(2\pi i \xi X_3) dX_3$$

$$= \frac{1}{1 + 2\pi i \xi \beta_T} \quad (63)$$

3.2. Analysis

Rapid evaluation of the deconvolution and error indicators can be achieved by applying the FFT algorithm. Figure 2 shows an example of the deconvolution of (i) $K\alpha_2$ peak, (ii) axial-divergence and (iii) flat-specimen aberrations, from the whole diffraction data of a LaB$_6$ sample.

A commercial diffractometer (RIGAKU RAD2-C) with a CuK$\alpha$ tube as the X-ray source was used for the measurement. The open angle of divergence and scattering slits was $\phi_1 = 1^\circ$ and a couple of Soller slits to restrict the axial divergence with nominal FWHM of $\phi_a = 2.5^\circ$ was used. The data shown in Fig. 2 were collected at the interval of 0.02$^\circ$ step, and include 6550 sampling points. Interpolated data with 65536 points were temporarily created for the deconvolution process.

Even though quite large number of data is simultaneously processed, all the calculation have been finished within several seconds on a personal computer (Apple iBook, PowerPC G3, 500 MHz).

Figure 3 shows how the diffraction peak profiles are changed on each deconvolution process for the 100, 321, 510-reflections of LaB$_6$ sample on magnified scales. The raw data are shown in Fig. 3(a) and the errors based on counting statistics are shown in Fig. 3(b).

Figure 3(c) shows the results of elimination of $K\alpha_2$ peak by the deconvolution method. The shoulder structure on the higher angle side of the main peak of the 100-reflection is removed, and the asymmetric profile of the 100-reflection is rather emphasized. The separated $K\alpha_2$ peaks are also successfully removed, as can be seen in the peak profiles of 321 and 510-reflections.

Figure 3(d) shows the results of further deconvolution of axial divergence effect. Significant change appears in the peak profile of the low-angle 100-reflection. The heavily asymmetric profile in Fig. 3(c) becomes fairly symmetric and sharpened shape in Fig. 3(d). The longer tail on the higher angle side of the 510-reflection in Fig. 3(c) is also reduced in Fig. 3(d). The results are both reasonable, because the longer tail caused by the axial divergence aberration is theoretically predicted on the lower angle side for the low-angle reflections and on the higher angle side for the high-angle reflections [13].

![Fig. 2. Deconvolution of whole powder diffraction data. (a) The raw diffraction profile of a LaB$_6$ powder sample; (b) the result of deconvolution, where spectroscopic $K\alpha_2$ subpeak, axial divergence and flat-specimen aberrations are eliminated.](image-url)
Figure 3(e) shows the results of elimination of the flat-specimen effect. Changes in peak profiles are not significant, but small shift of the peak position is found for the low-angle 100-reflection. It has been known that the experimental peak position is shifted to the lower angle by the effect of flat-specimen aberration. The result suggests that such a systematic error can be automatically corrected by applying the deconvolution. It can be confirmed that all the peak profiles in Fig. 3(e) are singlet, more symmetric and sharpened as compared with the raw data in Fig. 3(a).

Figures 3(f) and (g) show the range of the error indicators \( \pm \delta_n \) and \( \pm \varepsilon_n \), for the deconvoluted data shown in Fig. 3(e). It has been found that the values of \( \delta_n \) and \( \varepsilon_n \) are considerably affected by the numerical treatment of the boundary on the Fourier calculation. It seems that \( \delta_n \) is more reasonable as an error indicator for the deconvoluted data, while \( \varepsilon_n \) tends to overestimate the errors, as compared with the amplitude of the noisy structure in the deconvoluted intensity profiles.
4. Conclusion

A new approach to eliminate the effects of spectroscopic properties of the source X-ray and instrumental aberrations of powder diffractometers is presented. The method is based on the precise theoretical expressions of the instruments and the convolution theorem. An efficient numerical evaluation of deconvolution is achieved by applying fast Fourier transform technique. The method would be particularly useful for microstructure evaluation based on precise peak profile analyses.

References