A Comparison of Two Smoothing Methods as Pre-Processing for Iterative Deconvolution

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In order to solve the problem of noise enhancement in deconvolution, we studied the effects of smoothing on iterative deconvolution using two typical smoothing methods; the weighted moving average method and the spline functions fitting method. From the results of computer simulations, it is ascertained that the spline functions fitting method is superior to the weighted moving average method in noise reduction and resolution enhancement. The application of the spline method to real x-ray fluorescence spectra is shown, and is compared with the results obtained using the weighted moving average method.

1. Introduction

In x-ray fluorescence spectroscopy, highly resolved spectra are obtained by using a two-crystal spectrometer.^{1,2)} In such spectra, the measured profile is often dominated by the natural width and fine structures within this width are smeared. It is therefore necessary to use the resolution enhancement technique or the deconvolution method to obtain a well-resolved spectral line distribution.

However, a recognized problem in deconvolution is that noise components are amplified during the numerical data processing. It is therefore important for input data to have a very high signal to noise (S/N) ratio. Thus raw spectra almost always need smoothing. When using the weighted moving average

(Savitzky and Golay) method,³⁾ there is a difficulty in compromising between S/N ratio enhancement and distortion of the profile. In a previous paper,⁴⁾ we have shown that the spline functions fitting method gives rather smoother profiles with less deformation than Savitzky-Golay (S-G) smoothing method.

In this work, we used computer simulations to study the effects of smoothing as pre-processing for iterative deconvolution using these two typical methods.

2. Smoothing by Spline Functions

By the spline functions fitting method, a measured spectrum $M(x)$ is represented as a linear combination of B-splines;⁵⁾

$$M(x) = \sum_{i=1}^{n+m} c_i N_{mi}(x) \quad (1)$$

$$N_{mi}(x) = (g_i - g_{i-m}) M_{mi}(x) \quad (2)$$

where $N_{mi}(x)$ is the normalized B-spline, $M_{mi}(x)$ is the B-spline and g_i s are knots. The lower case letter m represents the order of B-splines. That is, a B-spline $M_{mi}(x)$ is a polynomial of $m-1$ degree within the interval (g_{i-m}, g_i) and equals to 0 outside of this interval.

The coefficients c_i s ($i=1, \dots, n+m$) are determined by the least squares method to fit the measured data. When using this method, the problem is how to determine the position of knots. We used the improved successive division method⁹. In addition, it is important for the knots not to be closely positioned. This is because closely distributed knots cause undulations in the processed results. Close distribution of knots must therefore be avoided. In order to fulfil this requirement, the minimum interval between two successive knots in the successive division procedure was set to as 5. The details of the fitting procedure are described in our previous paper.⁴⁾

3. Pseudo Deconvolution

By van Cittert's pseudo deconvolution, high frequency components, which are composed almost of noise, are amplified by $n+1$ after n -th iteration.⁶⁾ In order to avoid such noise amplification, van Cittert's method has been improved by several authors. Kashiwakura and Gohshi introduced S-G smoothing in the iterative procedure.^{6,7)} Kawata and Ichioka studied the convergence problem of the iterative deconvolution and solved this problem by the reblurring procedure.⁸⁾ Wertheim constructed the smoothing filter from the iterative procedure and incorporated it into the deconvolution process⁹⁾. In these methods, a low-pass filter is applied to suppress noise amplification.

We used the method by Kashiwakura and Gohshi which is termed the modified van Cittert's method and is represented in a mathematical form as follows;^{6,7,10)}

$$T_n(x) = T_{n-1}(x) - \{T_{n-1}(x) * L(x) - T_0(x)\} * S(x)_n^{-1}, \quad (3)$$

where $T_n(x)$ is the n -th processed spectrum, $T_0(x)$ is initial spectrum, $L(x)$ is the smearing function, $S(x)$ is the Savitzky-Golay's smoothing function³⁾ and the symbol $*$ represent the convolution integral. By this method, the transfer function for n -th iteration $T_n(w)$ is represent-

ed in the frequency domain as follows (there are some errors in the expression given in Ref. 10 and the following expression is correct);

$$T_n(w) = \frac{1 - (1 - L(w)) \left(\prod_{i=0}^{n-1} (1 - L(w)S(w)^i) \right)}{L(w)}, \quad (n \geq 1) \quad (4)$$

where $T_n(w)$, $L(w)$ and $S(w)$ are the Fourier transform of $T_n(x)$, $L(x)$ and $S(x)$ respectively.

In addition, Kashiwakura and Gohshi pointed out that successive deconvolution is very efficient for the iterative deconvolution and it reduces computation times. Successive deconvolution means that the smearing width is decomposed into several parts and deconvolution is performed by such decomposed width several times successively. In this paper successive deconvolution was performed according to the procedure described above using the Lorentz function, whose width is equal to one 4-th of the total width of the smearing. This procedure was therefore repeated 4 times. The Savitzky-Golay's filter function⁹⁾ was used as the smoothing function $S(x)$. The width of this filter was determined so as to be equal to the full width at half maximum (FWHM) of the processed result.

4. Results

As simulation test data, we used Lorentzian profiles with a Gaussian noise distribution. From the point of view of experiments, the practically limiting value of the peak intensity is 10^6 and in such cases the error becomes the order of 0.1% which is thought to be a lower limit. On the other hand, the S/N ratio of spectra with less than 1000 peak intensity is too low and they are not suitable for deconvolution. Therefore we fixed the peak intensity of test data to 10000 counts. However the results obtained are not peculiar to 10000 peak counts. In order to simulate actual spectra, noise was added with an amplitude proportional to the square root of the total number of counts in each channel. The test data therefore included about 1.0% noise at the peak intensity. The FWHM was 20 channels, and the total number of channels was 256. These values were also determined according to

Fig. 1. Processed results for 5-points S-G smoothed test data are shown with a noise-free Lorentzian. These test data are constructed from a Lorentz curve (peak intensity=10000 counts, FWHM=20 channels, peak position=160 channel) including noise whose distribution is Gaussian. The degrees of deconvolution are 50% and 80%. The achieved degree is shown in parentheses.

Fig. 2. Processed results for spline fitted test data are shown with a noise-free Lorentzian. These test data are the same as used in Fig. 1. The degrees of deconvolution are also the same as in Fig. 1 and the achieved degree is shown in parentheses.

actual spectra. This test data was first smoothed, and then deconvoluted.

Figs. 1 and 2 show the deconvoluted results for S-G smoothed data and spline fitted data respectively. In the case of S-G smoothing, the extended version by Proctor and Sherwood¹¹⁾ which is thought to be best optimized is used. When fitting with spline functions, 4-th order B-splines are used. Deconvolution from 20% to 90% was made by 10% steps. The number of iterations of deconvolution was determined by minimizing the residual sum of squares (RSS) between $T_0(x)$ and $T_n(x)*L(x)$. When these results are compared, the differences between the two methods are clearly seen. With the spline method, the processed results show a smoother profile, especially in the low intensity region, and the magnitude of the sidelobes is smaller.

Fig. 3 shows the RSS between the processed result and the ideally deconvoluted curve, and also the errors in FWHM for various degrees of deconvolution. The error of FWHM is determined by $(W_r - W_i)/(W_o - W_i)$, where W_o , W_r and W_i are the FWHM of the original spectrum, the deconvoluted spectrum and the ideally deconvoluted spectrum respectively. The error in FWHM is relatively small when the width of deconvolution is less than 40%,

Fig. 3. Errors of deconvolution for various deconvolution degrees. a) Residual sum of squares (RSS). b) Errors of FWHM.

Fig. 4. Results for Mn K $\beta_{1,3}$ spectrum of KMnO₄. Mn K $\beta_{1,3}$ spectra in Figs. 4 and 5 were measured by a two-crystal spectrometer (Toshiba AFV-701) using Si(220) as the analyzing crystals. Peak position=6488.8 eV, FWHM (measured)=3.80 eV, FWHM (deconvoluted, spline)=1.94 eV, FWHM (deconvoluted, S-G)=2.23 eV.

Fig. 5. Results for Mn $K\beta_{1,3}$ spectrum of MnF_2 . Peak position=6491.8 eV, FWHM (measured)=3.11 eV, FWHM (deconvoluted, spline)=1.64 eV, FWHM (deconvoluted, S-G)=1.58 eV.

but it becomes larger as the width of deconvolution exceeds 50%. The RSS almost converges to a constant value, as the width of deconvolution exceeds 40%, the value being 0.4×10^{-2} for the spline fitted data, and 0.5×10^{-2} for the S-G smoothed data, after normalization to unity with respect to the peak intensity.

We applied the modified van Cittert's method to real x-ray fluorescence spectra, that is, to the Mn $K\beta_{1,3}$ spectra of $KMnO_4$ and MnF_2 . Figs. 4 and 5 show the processed results for $KMnO_4$ and MnF_2 respectively, and compare the deconvoluted result using the spline fitted spectrum with that obtained using the S-G smoothed spectrum. The number of iterations for S-G smoothing was determined by the simulation results.⁴⁾ That is, 5-points S-G smoothing was repeated 50 times for MnF_2 (about 4000 peak counts) and 70 times for $KMnO_4$ (about 2400 peak counts). The natural width is about 1.6 eV for the Mn $K\beta_{1,3}$ line, and 4 successive deconvolutions were performed, each deconvoluted width being 0.4 eV. Since the FWHM of the measured spectra is about 3.9 eV for $KMnO_4$ and about 3.2 eV for MnF_2 , the degrees of deconvolution are about 40% and 50% respectively. As is shown clearly in Figs. 4 and 5, the spline fitted spectra give better resolved structures with fewer spurious peaks than do the S-G smoothed spectra. We

will make the interpretation of these structures our next subject of investigation.

5. Discussion

We have shown that the spline functions fitting method reduces structures due to noise in the iterative deconvolution much more effectively than does the S-G smoothing method. In this work, the number of iterations for S-G smoothing was determined so as to minimize errors due to smoothing. This results in insufficient noise reduction. When using more points in S-G smoothing, the S/N ratio increases and spurious structures in the deconvoluted results are reduced.

However, at the same time, the enhancement of resolution by deconvolution is also reduced. By using the spline fitting method, this problem, i.e. the compromise between resolution enhancement and reduction of spurious structures, can be satisfactorily solved. This is because of the properties of spline functions. That is, a m -th degree B-spline is a $m-1$ th order polynomial in the interval (g_{i-m}, g_i) . Therefore the derivative of order $m-1$ is a constant function and the derivative of order m is equal to 0 except for knot positions.

In Fig. 6, the derivatives of order 4 for a spline fitted spectrum and for a S-G smoothed spectrum are shown. In the case of the spline fitted spectrum, the derivative of order 4 be-

Fig. 6. Comparison of 4-th order derivative of spline fitted spectrum with that of S-G smoothed spectrum. The original spectra are the spline fitted Lorentzian and the S-G smoothed Lorentzian which are used in Figs. 1 and 2. Result for S-G smoothed spectrum is drawn with its base line being raised by 50.

comes almost 0 except for the peak region. On the other hand, the derivative of order 4 for the S-G smoothed spectrum shows non-zero values. Since the deconvolution procedure is equivalent to the linear combination of derivatives,¹²⁾ using the spline fitted spectrum as a original spectrum means that the higher derivatives than 4 are automatically cut off. This explains the efficiency of using spline functions as a smoothing method for the iterative deconvolution.

However it must be noted that the continuity of the spline fitted spectrum depends on the degree of B-splines used⁶⁾. When knots are not multiplied, the spline fitted spectrum obtained using m -th degree B-splines and their derivatives of the orders 1, 2, ..., $m-2$ are continuous, and the $m-1$ th derivative shows discontinuities at the knots. Therefore when a data point coincides with the position of a knot, discontinuity appears conspicuously when deconvolution is performed. In this paper, we used 4-th degree B-splines or piecewise cubic

splines. The processed result therefore has a second continuous derivative, except for points with multiple knots. That is, at points with nonmultiple knots a third derivative shows discontinuities. Hence the position of a knot must be shifted so as not to coincide with data points.

In conclusion, we have shown that fitting original data using B-spline functions reduces the spurious structures which often tend to appear in the deconvoluted result. This characteristic, i.e. fewer spurious structures, enables us to compare deconvoluted results with theoretical fine structure calculations.

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