Determination of common peak structure from multiple X-ray photo-electron spectroscopy data sets

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ABSTRACT
X-ray photo-electron spectroscopy (XPS) peak structure (i.e. peak parameters and the number of peaks) offers critical insights in chemical analysis of materials. Reference XPS spectral data are available for single-phases of compounds, as cited in various research papers and databases. Herein, we consider how individual peak structure varies among different reference spectra for the same single-phase of a compound. We developed a technique that automatically estimates common peak structures from multiple spectral data sets. Specifically, we developed a peak separation method that considers both common peak parameters and measurement-derived fluctuations. The proposed method can uniquely estimate the common peak structure of multiple XPS spectral data sets. For example, we applied the proposed approach to Ti 2p XPS results for TiO₂ from 15 previous reports. In this way, we confirmed that estimated structure has high interpret-ability.

KEYWORDS
X-ray photo-electron spectroscopy; automatic peak separation of multiple-spectra; sparse-modeling; Bayesian information criterion; genetic algorithm

CLASSIFICATIONS
Materials data analysis

1. Introduction
X-ray photo-electron spectroscopy (XPS) is a method for analyzing elements and compounds present at the surface of a material. Thus, XPS is widely used in material development and quality control. Analysis of XPS data requires assignment of peak structure (i.e. the peak parameters and number of peaks). Previous studies have developed fitting methods to automatically infer peak structures from individual spectral data [1–5]. In particular, a method proposed by Shinotsuka and co-workers efficiently estimates the number of peaks and peak parameters based on Bayesian information criterion (BIC) [6]. The estimated peak structure depends on the measurement environment (e.g. the analyzer’s energy resolution, X-ray beam density, charge neutralization, and sample mounting), the spectral statistical noise, and the surface condition of the sample. For example, Figure 1 shows 15 Ti 2p XPS spectral data of TiO₂ from various literature [7–19]. As shown in Figure 1, the variation in peak position and width is high due to factors in the measurement environment. Also, Figure 3 shows peak separation results estimated by applying the previous method to each of the 15 sets of spectral data in Figure 1. As shown in Figure 3, the optimally estimated number of peaks K depended on the spectral data despite all data deriving from the same single-phase compound species. We show a more detailed discussion of the above in section 3.1. Therefore, we can assign non-identical peak structures based on
common features of previously reported XPS spectral data from the same kind of compound. The best common peak structure should be estimated from multiple XPS spectral data sets, obtained from measurements of the same kind of sample. Here, we develop a method to identify the best common peak structure that uniquely characterizes the material and is unaffected by differences in the environment, such as the operator and measuring machine. This is a particularly important issue for analyzing and comparing experimentally obtained XPS spectra with reference spectra cited in databases. The assignments may be unreliable if we focus on a single set of reference data of a single-phase chemical compound.

Here, we propose a method of uniquely and automatically determining the best common peak structure that integrates all single-phase XPS literature data. The proposed method simultaneously estimates common peak parameters from multiple XPS spectral data sets from a single-phase compound and fluctuations depending on the different measurement environments. We interpret the method as sparse modeling because it represents various XPS spectra composed of many data points with a few common peak parameters. Notably, the proposed framework does not select the best quality spectrum from all the spectra but, rather, estimates the best common peak structure that effectively generalizes all the spectra.

2. Method

We aimed to uniquely and automatically estimate common peak parameters \( \theta \) (e.g. peak height \( h \), peak position \( p \), natural width \( y \)) of XPS spectra for single-phase compound. We reasonably assumed that all collected spectral data would have common peak parameters \( \theta \) and the same number of peaks \( K \) because they were obtained from experimental measurements of the same single-phase compound. In reality, spectral data fluctuate in terms of peak position and peak shape result from the measurement environments. This study proposes a peak separation model that parameterizes the common peak \( \theta \) and measurement-derived fluctuation \( \delta \) parameters.

2.1. Formulation of peak separation of a single spectrum

Figure 2 shows the relationship between the observed XPS spectrum affected by the measurement environment and the common peak structure, which was not directly observed. The formulation of a peak separation model, as shown in Figure 2, is as follows. We assumed that the common peak structure described as the common peak parameters \( \theta \) yields ideal spectral data, as shown in Figure 2(a). We assumed that common peaks is represented Lorentz function. Thus, we formulate the common peak structure as the following multiple Lorentz function \( c(x_n : \theta) \):

\[
c(x_n : \theta) = c(x_n; h, p, y),
\]

\[
= \sum_{k=1}^{K} h_k L(x_n; p_k, y_k),
\]

where \( \{(x_n, y_n)\}_{n=1}^{N} \) is input spectral data, and \( n \) is the index of the sample. The parameter \( K \) is the number of peaks, and \( k \) is its index. The function \( L(x; p, y) \) is Lorentz function, where \( \theta = \{h, p, y\} \) represents the common peak parameters in the XPS data of a single-phase compound. The parameters \( h = \{h_k\}_{k=1}^{K} \), \( p = \{p_k\}_{k=1}^{K} \), \( y = \{y_k\}_{k=1}^{K} \) correspond to individual peak heights, positions and natural widths, respectively.
We can only observe spectra that were affected by perturbation due to the device. As shown in Figure 2(b), we assume the observed signal spectrum \( s(x_n; \theta, \delta) \) as a parametric perturbation of the common peak structure \( c(x_n; \theta) \), where \( \delta \) represents the perturbation parameters from measurement-derived fluctuations. And, the perturbation of peak widths is represented by a convolution-operation with a Gaussian function \( g(\cdot) \) [20]. Thus, we define the observed signal spectrum as follows:

\[
s(x_n; \theta, \delta) = \int_{-\infty}^{\infty} G(x'; \eta h, p + \mu, \sigma) c(x_n - x'; \eta h, \mu, \sigma) dx',
\]

(3)

\[
= \sum_{k=1}^{K} \eta h_k V(x_n; p_k + \mu, \gamma_k, \sigma_k),
\]

(4)

where the function \( V(x; p, \gamma, \sigma) \) is Voigt function, the function \( G(x; h, p, \sigma) \) is a multi-modal Gaussian function \( \sum_{k=1}^{K} h g_k(x; p_k, \sigma_k) \), the measurement-derived fluctuation parameters \( \delta = \{ \eta, \mu, \xi, \tau_k \ (k = 1, \ldots, K) \} \). The parameters \( \eta, \mu, \xi, \) and \( \tau_k \) are the fluctuation of peak height, peak position, peak width, and device width from thermal vibration as Gaussian components, respectively. Peak widths of Gauss component \( \sigma_k \) can be expressed \( \sigma_k^2 = \xi^2 + \tau_k^2 \) because it is a convolution operation between two Gaussian functions. The observed data point \( y_n \) is represented by an analytical model \( f(x_n; \theta, \delta, a, b) \):

\[
y_n \approx f(x_n; \theta, \delta, a, b)
\]

(5)

where the analytical model \( f(x_n; \theta, \delta, a, b) \) is represented by the linear sum of the signal spectrum \( s(x_n; \theta, \delta) \) and the background \( b(x_n; a, b) \):

\[
f(x_n; \theta, \delta, a, b) = s(x_n; \theta, \delta) + b(x_n; a, b)
\]

(6)

\[
= \sum_{k=1}^{K} \eta h_k V(x_n; p_k + \mu, \gamma_k, \sigma_k) + b(x_n; a, b),
\]

(7)

where \( b(x_n; a, b) \) is the background modeled by the Shirley method [21–23]. The parameters \( \{a, b\} \) are two end point intensities of the background. The signal spectrum \( s(x_n; \theta, \delta) \) is expressed on the basis of the common peak structure \( c(x_n; \theta) \).

2.2. Formulation of peak separation of multiple spectra

This section extends the unified peak separation model in the above section to model collected spectral data from the same kind of single-phase compounds. We assume that all collected spectral data have the same common peak parameters \( \theta \) and the same number of peaks \( K \) because they were obtained by measurements from the same kind of compounds. Therefore, the proposed method estimates \( \theta \) and \( K \) as common peak parameters in \( M \) spectral data \( \{D_m\}_{m=1}^{M} \). In the \( m \)-th spectral data \( D_m = \{(x_{mn}, y_{mn})\}_{n=1}^{N_m} \), data point \( y_{mn} \) is expressed as follows by Equation (5) as a set of measurement-derived fluctuation parameters \( \delta_m \):

\[
y_{mn} \approx f(x_{mn}; \theta, \delta_m, a_m, b_m),
\]

(8)

where \( y_{mn} \) is the intensity of data-point \( n \) in the \( m \)-th spectral data, \( x_{mn} \) is the binding energy of the data-point \( n \) in the \( m \)-th spectral data, \( N_m \) is the number of data point in the \( m \)-th spectral data, the parameters \( \{a_m, b_m\} \) are two end point intensities of the background.

The present study proposes a simultaneous peak separation method for multiple XPS data sets of the same single-phase compound. The model for estimation of the peak structure is expressed as follows:

\[
f(x_{mn}; \theta, \delta_m, a_m, b_m) = s(x_{mn}; \theta, \delta_m) + b(x_{mn}; a_m, b_m).
\]

(9)
The signal spectrum \( s(x_{mn}; \theta, \delta_m) \) is expressed as follows:

\[
s(x_{mn}) = \int_{-\infty}^{\infty} G(x'; \eta_m h, p + \mu_m, \sigma_{mk}) c(x_{mn})
- \times \eta_m h, p + \mu_m, y) dx'
\]

\[
= \sum_{k=1}^{K} \eta_m h_k V(x_{mn}; p_k + \mu_m, y_k, \sigma_{mk}),
\]

where \( K \) shows the number of peaks and \( k \) means its index. The parameters \( \delta_m = \{ \eta_m, \mu_m, \zeta_m, \tau_{mk} \} \) are parameters to compensate for changes in the spectral shape depending on the measurement environments \( m \). The parameters \( \eta_m, \mu_m \) and \( \sigma_{mk} \) represent fluctuations of the peak height, peak position, and peak width, respectively. The parameters \( \theta = \{ h, p, y \} \) are common peak parameters in all collected spectral data \( \{ D_m \}_{m=1}^{M} \).

Here, the estimated overall parameters are \( \beta = \{ \theta, \delta, a_m, b_m \} \), and we determine \( \beta \) such that the error function \( E(\beta) \) is minimized. The error function \( E(\beta) \) is expressed as follows:

\[
E(\beta) = \frac{1}{N} \sum_{m=1}^{M} \sum_{n=1}^{N_m} \left( y_{mn} - f(x_{mn}; \beta) \right)^2, \tag{12}
\]

\[
\hat{\beta} = \arg \min_{\beta(\beta)} \{ F_{BIC}(\beta) \}, \tag{15}
\]

where \( \hat{\beta} \) is the best overall parameter, \( \hat{K} \) is the upper number of peaks, \( \beta(\beta) \) is the optimized overall parameter sets with number of peaks \( K \). The factor \( \lambda(\beta) \) is the number of parameters in the parameter sets \( \beta(\beta) \), and \( \lambda(\beta) \) increases in proportion to the number of peaks \( K \). The BIC reasonably selects analysis results with a lower error and a smaller number of peaks.

### 3. Results and discussion

Figure 1 shows 15 Ti 2p XPS spectral data of TiO\(_2\) from 15 literatures [7–19] and the present study applied the proposed method to those spectral data. As shown in Figure 1, the variation in peak position and peak width is roughly described by differences in the calibration of the energy axis and in the energy resolution, respectively.

Figure 3 shows peak separation results estimated by applying the previous method (i.e. individual-fitting) to each of the 15 sets of spectral data in Figure 1. As shown in Figure 3, the optimally estimated number of peaks \( K \) depended on the spectral data despite all data deriving from the same single-phase compound species. These results indicate that the estimated individual peak structure depends on the measurement environment.

#### 3.1. Comparison with single spectral peak separation

In contrast to the previous method (Hereinafter referred to as the individual fitting) [5], the proposed method provides a common peak structure with an optimal number of peaks from multiple spectral data. For example, Figures 4 and 5 compares the peak separation results with \( K = 5, 4 \) estimated by the individual-fitting and the peak separation results with fixed \( K = 2 \) estimated by the proposed method from two original spectra, as shown in Figure 3(n,b). Here, Figures 4(n)-1 and 5(b)-1 are identical to Figure 3(n,b), respectively. Figure 4(n)-1, (n)-2 are peak separation results with different numbers of peaks \( K \) estimated by individual-fitting and by the proposed method.

In the case of individual spectral peak separation, the number of peaks is often over-estimated than the proposed method because applications to other spectral data are not considered. As shown in Figure 4(n)-1, the
individual-fitting estimated five peaks. In contrast, as shown in Figure 4(n)-(2), the proposed method estimated two peaks based on 15 spectral data sets. Figure 4(n)-(1), (n)-(2) show peak separation results with similar residuals. We deduced that the proposed method has a high generalization performance for other spectral data of the same compound realized by adjusting the fluctuation of the spectral shape depending on the measurement device. In contrast, the comparison between Figure 5(b)-(1) with small residuals and Figure 5(b)-(2) with large residuals suggests that the proposed method’s generalization performance was not completely satisfactory for some spectra. Therefore, it was suggested that the spectral data having large residuals included fluctuation of peak shape depending not only on the measurement device but also on the measured sample.

3.2. Variability of measurement-derived fluctuation parameters

The proposed method also estimated measurement-derived fluctuation parameters $\delta$, and thus allowed us to evaluate the variability of peak position and peak
width depending on the measurement environment. Figure 6 shows the variability of (a) peak position and (b) peak width (half width at half maximum, HWHM) at the main peaks of the $\mathrm{Ti}_{2p_{3/2}}$ which are present in Figure 3. The dashed lines in Figure 6(a,b) show the common peak position and the common peak width of common peak structure parameters $\theta$ for the $\mathrm{Ti}_{2p_{3/2}}$ main peak, respectively. The given $M = 15$ spectral data sets had a variability of 458.0–459.4 eV in peak position and of 0.3–0.6 eV in HWHM.

In Figure 6(a), the red line is the band-gap value (3.2 eV) for $\mathrm{TiO}_2$ [28]. The main peak fluctuation was within the band-gap value for $\mathrm{TiO}_2$. Thus, the energy calibration of 15 reference spectra was reasonably performed because the Fermi-level of $\mathrm{TiO}_2$ is pinned within the band-gap.

3.3. Estimation of common peak structure from multiple XPS data sets

Figure 7 shows BIC values when analysis under the peak number $k$, which were estimated from 15 spectral data set by the proposed method. In this study, we set upper number of peaks to four. The smallest BIC in Figure 7 gives the best peak number $K = 2$ and the best overall parameter $\hat{\beta}$ from all multiple spectral data. The $\mathrm{Ti} 2p$ XPS spectral data of $\mathrm{TiO}_2$ are often simply expressed by two peaks in references [18,29–33], which are separated by the spin-orbit splitting energy. The proposed method automatically estimated the same number of peaks, as determined by expert analysis. The computation time of the proposed method was 54 [minutes] and the computational
spec was AMD Ryzen Thread ripper 3990X (64 core, 128 thread), 256GB DDR4-3200/PC4-25600SD, Ubuntu 18.04.5 LTS.

Figure 8 shows the peak separation results obtained by applying the best overall parameter $\beta$ with the best peak number $K = 2$ to $M = 15$ raw spectral data sets in Figure 3. As shown in the residual spectra of Figure 8, the common peak structure parameter $\theta$ represented the 15 spectral data sets satisfactorily for practical use by modeling the fluctuation depending on the measurement environment.

Figure 9(a,b) respectively show the superimposed 15 math functions of Figure 3 obtained by applying individual-fitting to the 15 spectral data sets and common peak structure estimated by the proposed method from 15 data sets. In Figure 9(b), dot line shows the common peak structure, and solid line shows the typical signal spectrum based on common peak structure. The typical signal spectrum was made by convolution process of the common peak structure with a Gaussian function. The width $\sigma$ of the Gaussian function to be convoluted was set to 0.54 so that the area ratio of the split peaks after the

Figure 7. BIC values each number of peak $K$, which were estimated from 15 spectral data sets shown in Figure 1 based on the proposed method. Data points correspond to the results of 15 peak separations.

Figure 8. Simultaneous peak separation results applying the proposed method to 15 spectral data. Data correspond to point of the lowest BIC value in Figure 7. $M = 15$ spectral data sets are represented by the best peak number $K = 2$. Black lines at the bottom are the residuals between the fitting and the spectral data. (a)-(o) correspond to the same spectral data in Figure 1.
Figure 9. Peak structures based on estimated parameter set [(a) superimposed 15 math functions of Figure 3 obtained by applying the individual-fitting to each of the 15 data sets (b) common peak structure estimated by the proposed method from 15 data sets. Dot line is the common peak structure, and solid line is typical signal spectrum based on common peak structure. This result corresponds to data point having the lowest BIC value in Figure 7. Best common peak structure is represented by two peaks].

convolution process would be the theoretical value. This result corresponds to data point having the lowest BIC value. The data shown in Figure 9 are normalized. We conclude that the common peak parameters $\theta$ in Figure 9 (b) based on integrated analysis of multiple XPS spectral data sets generalize and simplify the spectral data in Figure 9(a).

The theoretical area ratio of the 3/2 peak to the 1/2 peak in the XPS spectra of 2p orbitals is 2.0 [34], which not matched the area ratio of Lorentz component in Figure 9(b) of 1.2. In spectral data-set of TiO$_2$ used in this study, it is suggested that unobserved original peaks contains not only the Lorentz component but also the Gaussian component due to physical factors, e.g. the thermal vibration of crystal lattice [35], the heterogeneity of the sample, and so on.

This proposed method also provides a reference peak structure for a single-phase compound in analysis of XPS data from multi-phase compounds. XPS spectral analysis is often performed by comparing spectra for mixed phase compounds with reference spectra of individual single-phase compounds. Typically, multiple XPS reference spectra are available for the same kind of compound and selection of the best one is not easy. Thus, there is a need to determine unique reference peak structures mathematically from the reference spectra. This is our motivation for developing the proposed method. We note that this method is realized by modeling reference spectral data with peak functions to remove statistical noise and calibrate the energy position and energy resolution [36].

The proposed method estimated not only the common peak structure parameters $\theta$ but also measurement-derived fluctuation parameters $\delta$ such that the proposed method allows quantitative evaluation of the variability of the peak position and peak width depending on the measurement. These values of the variability (for example, as shown in Figure 6) can be used to set up a search space in spectral analysis with single-phase spectra. Additionally, the proposed method can detect changes in spectral shape that depend on the measured sample.

4. Conclusion

We aimed to automatically determine the common peak structure in multiple XPS data sets for the same kind of single-phase compound. We formulated the analytical model by separating common peak parameters $\theta$ and measurement-derived fluctuation parameters $\delta$ from multiple XPS spectral data and estimated the best number of peaks based on BIC. The proposed framework is not a method of selecting the best quality spectral data of a single spectral data selected from multiple spectral data but rather a method of building the material-derived best common structures from multiple data sets. For example, we examined Ti 2p XPS reference spectra for TiO$_2$ cited from 15 reference articles and successfully derived the best common structure from these multiple spectral data. Therefore, formulating the proposed method with full Bayesian estimation is a future work.

In principle, we expect that the proposed method’s estimation-accuracy will increase as more data sets are added. This is a useful aspect of the proposed method when considering the construction of large-scale databases [37], as represented by materials informatics. From the viewpoint of informatics, the proposed method can be interpreted as sparse modeling that extracts essential structures.

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Appendix. Setting of analysis parameters

This section shows the setting of optimization by the genetic algorithms. We set the settings of the genetic algorithms as follows: individual number is 30, island number is 60, probability of cross-over is 0.8, probability of mutation is 0.1, generation number is 6000.

In the optimization by the genetic algorithms, we have to set the generation distribution of parameters. This section shows setting of analysis parameters in optimization. Note that the spectral data to be analyzed were normalized on a scale of 0–1. The following settings are common peak parameters $\theta$:

$h \sim \text{Uniform}(0.0, 1.0)$,

$p \sim \text{Uniform}(\min(x), \max(x))$,

$\gamma \sim \text{Gamma}(1.0, 4.0)$,

where $\text{Uniform}(\cdot)$ is the uniform distribution, $\text{Gamma}(\cdot)$ is the gamma distribution. The following settings are measurement-derived fluctuation parameters $\delta$:

$\eta \sim \text{Normal}(1.0, 0.1)$,

$\mu \sim \text{Normal}(0.0, 0.3)$,

$\xi \sim \text{Gamma}(1.0, 4.0)$,

$\tau \sim \text{Gamma}(1.0, 0.03)$,

where $\text{Normal}(\cdot)$ is the normal distribution. Here, we set the generation distribution of peak widths from thermal vibration $\tau$ to be small relatively. This is because peak widths due to thermal vibration $\tau$ is significantly smaller than peak widths due to device $\xi$. The following settings are parameters of the background:

$a \sim \text{Normal}(I_h, 0.05)$,

$b \sim \text{Normal}(I_l, 0.05)$,

where $\{I_h, I_l\}$ are intensities at the endpoints of measurement spectral data.