

Full automatic peak separation of X-ray photoelectron spectroscopy spectra

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In X-ray photoelectron spectroscopy, the peak separation of the measured spectra is essential to identify the compound species in the sample from the measured spectra. Currently, this peak separation process is not fully automated because of its manual selection of the initial values of each parameter (e.g., energy position, width and so on) of the peak. As a result, the solution of the peak separation is highly dependent on the manual operation, which causes a reproducibility problem. In this paper, we introduce the development of the algorithm, which requires full automation of the peak separation.

1. Introduction

X-ray photoelectron spectroscopy (XPS) is widely used in the field of material development as a method for identifying the compound species, the composition ratio, chemical bonding state, and electronic state of compounds in the surface layer of a sample. The presence of compound species in the sample evaluated by XPS is judged from the energy position and shape of the XPS spectrum consisting of one or more peaks unique to each compound. Therefore, peak separation is the most important in XPS data analysis. However, in the case of mixed samples consisting of a large number of compounds, the spectral shape becomes more complex and the results of the peak separation are strongly dependent on the initial values of each parameter of the peaks (binding energy, half-width, intensity, and Gaussian/Lorentzian mixture ratio in the pseudo-Voigt function) set by the analyst, causing problems in the reproducibility of the peak separation.

In order to ensure the reproducibility of the peak separation, it is necessary to describe in detail the XPS instrument configuration, the experimental conditions, the type of algorithm and software for the peak separation, and the initial parameters and constraints entered into the software during the peak separation. The reporting on this peak separation is described in ISO 19830 published in November 2015 (Surface Chemical Analysis - Electron spectroscopies - Minimum reporting requirements for peak

fitting in X-ray photoelectron spectroscopy), which we reported in our previous report^[1]. It should be noted, however, that this reporting, as specified in ISO 19830, does not fully guarantee the reproducibility of peak separation. The essential reason for the difficulty in fully guaranteeing the reproducibility is that the task of separating peaks containing statistical noise tends to give a local solution, which from a mathematical point of view corresponds to a nonlinear least squares solution dependent on the initial values at software runtime.

In this paper, we introduce an attempt at fully automatic peak separation without initial value dependence, which is a meta-heuristic approach to search for the optimal solution by changing the initial value.

2. How to automate XPS peak separation

2.1 Automatic peak and background separation

The first task in the peak separation of XPS spectra is to remove the background caused by inelastic scattering of photoelectrons as they travel through the sample. The Shirley method is usually used to remove the background in XPS because of its simplicity, but the usual Shirley method requires the manual setting of endpoints of the energy region to evaluate the background. In order to automate the Shirley method, the active Shirley method has been proposed to obtain the peak and background in a self-consistent manner considering their causal relationship^[2, 3]. The active Shirley method automatically adjusts the endpoints of the energy region of interest, so that the adjusted endpoints are ideally

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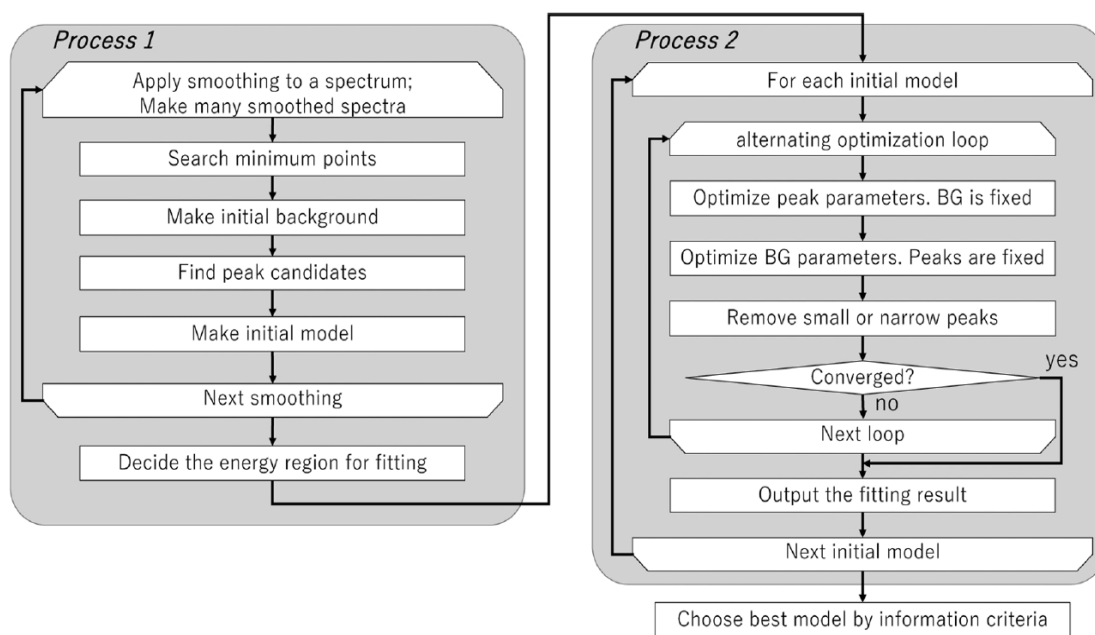


Figure 1 Flowchart of fully automatic peak separation of XPS spectrum ^[4]

The processes to automatically find the optimal solution of peak separation are 1) generation of a large number of initial peaks by varying the degree of smoothing, 2) self-consistent separation of peaks and background, and 3) selection of solutions based on the information criterion.

independent of the initial values. The removal method of the XPS background including the active Shirley method is described in ISO TR 18392 (Surface chemical analysis - X-ray photoelectron spectroscopy - Procedures for determining backgrounds).

2.2 Automatic search for solutions with varying initial peak values

A variety of number of peaks and initial values of the peak parameters (binding energy, width, intensity, and the mixture ratio of Gaussian/Lorentzian in the pseudo-Voigt function) gives many solutions of the peak separation of an XPS spectrum. The optimal solution is extracted from these solutions. We adopted a meta-heuristic method to change the initial values of the peak parameters by applying smoothing to the XPS spectra containing statistical noise (using the Savitzky-Golay algorithm) and gradually increasing the degree of smoothing. As the degree of smoothing is increased, the number of peaks decreases as an initial value. Figure 1 is a flowchart of the above processes.

The information criterion was used to find the optimal solution among the many solutions obtained in this way. The reason why the information criterion is used instead of the chi-square value is that the chi-square value tends to result in so-called overfitting, in which the experimental value is explained using an excessive number of peaks. To avoid this, an information criterion in which a penalty term is added as the number of peaks increases is used. The results are shown in Figure 2. Figure 2 shows the XPS valence band spectra of Polyvinyl methyl ketone, and the number of initial peaks obtained with varying degrees of smoothing, as well as the number of peaks in the solution that best explains the experimental values (after convergence of the gradient method), are evaluated using the Bayesian information criterion (BIC) in Figure 2(b). From this figure, when the number of peaks is three, the value of the BIC is the smallest, and it is judged to be the optimal solution. The result of the peak separation is shown by the solid line in Fig. 2(a). All the processes to find the optimal solution in Fig. 2(a) are performed automatically, and it is an important point in this

report to give the fully reproducible solution of the peak separation.

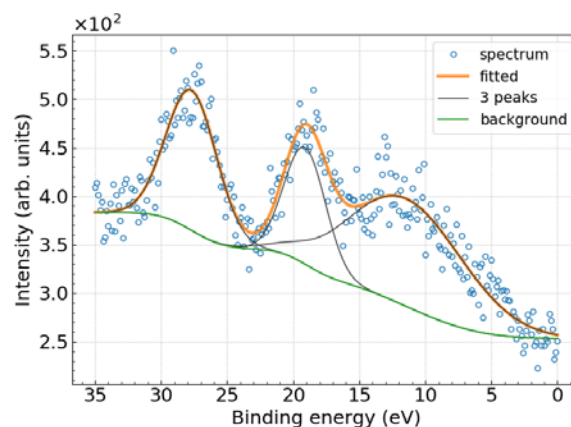
In addition to the BIC, we also used the Akaike Information Criterion as an indicator, but the BIC tended to give the optimal solution with a smaller number of peaks, and also gave an optimal solution that was close to the judgment of XPS experts, so we adopted the BIC as the more desirable indicator in this report.

This report provides an overview of the reference^[4] and is considered for future round-robin testing of XPS peak separation.

References

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(a)



(b)

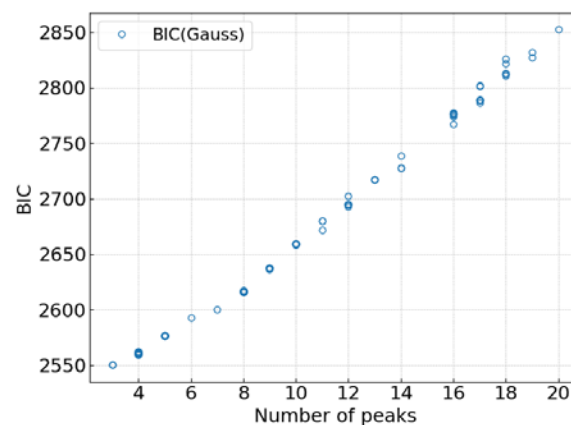


Figure 2 XPS spectral analysis of the valence band of polyvinyl methyl ketone^[4].

(a) XPS spectrum (blue dots) and optimal peak fitting solution (solid line). (b) Relationship between number of peaks and BICs of peak fitting solutions depending on the initial peaks. The optimal peak fitting solution (solid line in (a)) has minimum BIC at the peak number of 3 in (b).