Automatic Background Estimation of Spectra

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Automatic background estimation for XPS, AES and EDX spectra is attempted in order to make rapid qualitative and/or quantitative analyses. The start and end points of the background at both sides of each spectrum peak are obtained on a given algorithm. To link these start and end points, the background curve can be chosen from two methods: linear or Shirley. The selection of the methods gives not a negligible difference on the result of the quantitative analysis for a spectrum with high background.

1. Introduction

It has been made some attempts to estimate the background in the specified region of the XPS spectra using the Shirley method[1,2]. However, in this method one must specify the spectrum region to be estimated in advance, and it is not possible to estimate the background automatically for any type of spectra (XPS, AES, or EDX). This is in contrast to the Tougaad background[3] where the spectral region is automatically found by the algorithm. However, this method requires the spectrum to be recorded in a wide energy range. The Shirley and linear background can be applied to spectra taken over a small energy region around a peak. In this report, we propose a method for automatic background estimation by modified Shirley or linear methods of spectra of any kind by using only the spectrum shape and it's application to qualitative and quantitative analyses are discussed. The obtained results are found to be almost satisfactory for practical use.

2. Peak detection

There are several methods to find peaks in a spectrum, but they are generally categorized into two types: with or without second derivative curve of the spectrum. We will show the characteristics of the two methods briefly.

2.1 Direct peak detection

This method firstly assumes the background curve of a spectrum is generally gentle and the total spectrum region containing peaks is much narrower than the one without them, and then makes a rough estimation of the background intensity for each point of the spectrum. As the background intensity changes rather gently compared with the intensity near the peak, we assume that it can be expanded by using the $2m+1$ points of data which cover the region with several times of the average full width of half maximum of the peak, w. The background b_i ($i=1,\dots,T$), where T is the total sampling points, can be approximately written by using the spectral data y_i as follows:

$$b_i=\sum_{j=-m}^{m} h_j y_{i+j} \quad ,$$

where h_j is the coefficient of the simple moving average, and is expressed as

$$h_j=1/(2m+1)\,,$$

The variance of b_i is expressed as[4,5]:

$$\sigma_{bi}^{\ 2}=\sum_{j=-m}^{m} h_j^{\ 2}(Var)_{i+j}+2\sum_{j=-m}^{m}\sum_{l\neq j}^{m} h_j h_l (Cov)_{i+j,i+l}\,,$$

where, $(Var)_{i+j}$ is the variance of y_{i+j} and $(Cov)_{i+j,j+l}$ is the covariance of y_{i+j} and y_{j+l}. If the random nature of the spectrum data y_i is assumed, we have

$$(Var)_{i+j} = y_{i+j} .$$

Furthermore, assuming that each y_i is independent, and has no correlation with each other, we have

$$(Cov)_{i+j,j+l} = 0 .$$

Thus, the variance of b_i can be expressed as

$$\sigma_{bi}^2 = \sum_{j=-m}^{m} h_j^2 y_{i+j} = \frac{1}{(2m+1)^2} \sum_{j=-m}^{m} y_{i+j} .$$

Then, the variance of $n_i = y_i - b_i$ is estimated as

$$\sigma_{ni}^2 = \sigma_{yi}^2 + \sigma_{bi}^2 = y_i + \frac{1}{(2m+1)^2} \sum_{j=-m}^{m} y_{i+j} .$$

Therefore, the final inequality to decide a peak is given by using the critical value $k \fallingdotseq 2 \sim 3$ as

$$n_i > k\sigma_{ni} = k\sqrt{y_i + \frac{1}{(2m+1)^2} \sum_{j=-m}^{m} y_{i+j}} .$$

Or, in a more familiar expression,

$$y_i > b_i + k\,\sigma_{ni} . \qquad (2.1)$$

The local maximum y_i satisfying the inequality (2.1) is regarded as a peak (see Fig. 1).

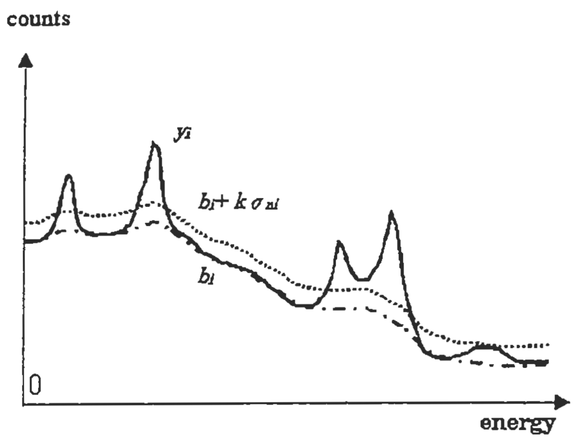

Fig. 1. Schematic diagram of y_i, b_i and $b_i + k\,\sigma_{ni}$.

2.2 Peak detection with 2nd derivative

In this case, the candidate peaks are detected by the following steps:

(1) Calculate the second derivative curve (e.g. by using Savitzky-Golay method[6]).

(2) Pick up the candidate peak positions at the local minimum (minus value) of the second derivative curve.

(3) Let p be a candidate peak position, and w be the average full width at half maximum of the peak in the original spectrum, where w is usually given in the peak detection condition (see Fig. 2). If a positive local maximum exists at $x = p_1$ in the second derivative spectral range, $p - 3w \leqq x < p$ in the nearest candidate peak (if it does not exist, the position, $p_1 = p - 3w$ is regarded as the position), p_1 is regarded as an intermediate position to the left-side background, and furthermore if a local minimum exists in the smoothed spectrum or a zero cross position in the second derivative spectrum at $x = q_1$ in the spectral range, $p_1 - 2w \leqq x < p_1$ in the nearest candidate peak (if it does not exist, the position, $q_1 = p_1 - 2w$ is regarded as the position), the value, $l_1 = p - q_1$ equals to the distance from the peak to the left-side background position $p - l_1$ with intensity B_1. Likewise, the right hand side background end position is easily determined by the same algorithm as mentioned above, giving the right hand side background position q_2 and intensity B_2.

(4) If the background curve near the peak can be approximated by a straight line, the background intensity B at the peak position is calculated as

$$B = (B_1 l_2 + B_2 l_1) / (l_1 + l_2).$$

If P is denoted as the peak intensity with the background, and N as the net peak intensity, then, $N = P - B$, and the variance σ_N^2 of N is given by

$$\sigma_N^2 = \sigma_P^2 + \sigma_B^2 ,$$

where

$$\sigma_P^2 = P,\ \sigma_{B1}^2 = B_1,\ \sigma_{B2}^2 = B_2, \text{and}$$

$$\sigma_B^2 = [l_2/(l_1+l_2)]^2 \sigma_{B1}^2 + [l_1/(l_1+l_2)]^2 \sigma_{B2}^2 .$$

Then, σ_N^2 is calculated as follows:

$$\sigma_N^2 = P + (B_1 l_2^2 + B_2 l_1^2)/(l_1+l_2)^2 .$$

Therefore, the peak decision condition is given as follows:

$$N > k\,\sigma_N \qquad (2.2)$$

Incidentally, in order to apply these procedures more effectively for the practical situations, some exceptional cases should also be taken into consideration. For example, some especially broad peaks do not satisfy the inequality (2.1). This problem is solved by including the broader temporary peaks with area greater than a certain minimum as real peaks. While, plural peaks or valleys sometimes appear above or under the threshold for the case of 2.1 or 2.2, respectively.

This problem is also solved by considering whether the peaks or valleys of the spectrum or the 2[nd] derivative curve exceed a certain limit of the variance of the spectrum noise[5].

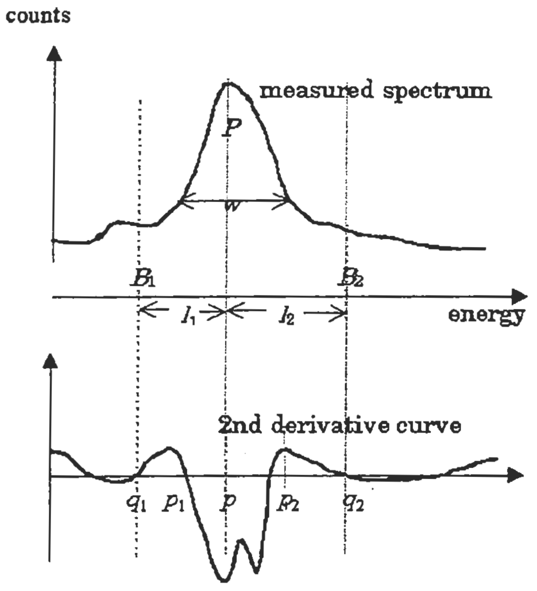

Fig. 2 Schematic diagram of peak and background positions.

3. Background Estimation and Subtraction

The background estimation is made under the following steps:

(1) Calculate the smoothing curve of the spectrum.

(2) Regard the smoothing curve as the background curve within the region without peak

(3) Let q_1 and q_2 be the start and end points of the background on the energy axis for a peak.

(4) Connect the end points (q_1, B_1) and (q_2, B_2) on the spectrum with a straight line (linear) or Shirley curve.

The background curve based on the Shirley method is calculated by the following way:

For the calculation of the background curve shown in Fig.3, we assume that there are n points between the end points of (q_1, B_1) and (q_2, B_2), and let the background and net peak intensities at the i-th point in the j-th approximation be $BG_j(i)$ and $N_j(i)$, respectively. Then,

$$N_j(i)=y_i-BG_j(i).$$

By using the Shirley's formula[1],

$$BG_j(i)=\frac{(B_1-B_2)Q_j(i)}{P_j(i)+Q_j(i)}+B_2 ,$$

where, $P_j(i)$ and $Q_j(i)$ are the left and right side of the net peak areas at the i-th point in the j-th approximation, and they are expressed as follows (assuming the step width being 1):

$$P_j(i)=\sum_{l=1}^{i} N_j(l)-0.5\left(N_j(1)+N_j(i)\right)$$

and

$$Q_j(i)=\sum_{l=i}^{n} N_j(l)-0.5\left(N_j(i)+N_j(n)\right)$$

For the 0-th approximation, the initial background curve $BG_0(i)$ is taken as the straight line connecting the 2 points (q_1, B_1) and (q_2, B_2). This iterative calculation continues until the following convergence condition is satisfied:

$$| S_j-S_{j-1} | /S_j<0.001 ,$$

where,

$$S_j=P_j(i)+Q_j(i) .$$

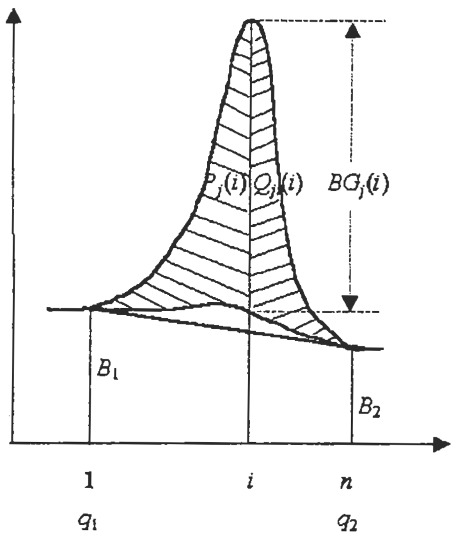

Fig. 3 Schematic diagram of the background subtraction by the Shirley method[1].

4. Qualitative Analysis

The qualitative analysis is made by the following steps:

(1) Assign each detected peak position with the corresponding transition lines.

(2) Determine the identified element from the information of the assigned transition lines and its intensity.

If n peaks are assigned to an element, the confidence of existence of the element C_E can be empirically given by the confidence of the existence of each peak C_{Pi} and the emergence probability of the transition line P_{Ti} as follows:

$$C_E \doteqdot \sum_{i=1}^{n} C_{Pi} P_{Ti}\ , \quad \text{where, } C_E=1, \text{ if } C_E>1.$$

If a peak is simultaneously assigned by the transition lines of other elements whose existences are certain, the sign of the P_{Ti} turns into minus. C_{Pi} is expressed by the function of k_i of the i-th peak satisfying the equation that is given by replacing ">" with "=" for the inequality (2.1) or (2.2), and the emergence probability of the transition line is considered to be given by the relative intensity of the line. Fig. 4 shows an example of this qualitative analysis for an AES spectrum.

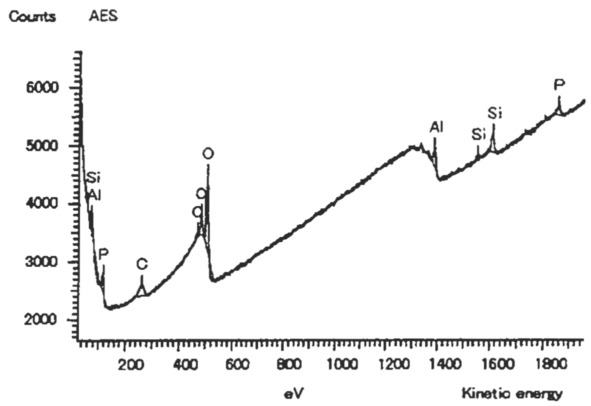

Fig.4 Result of a qualitative analysis for AES.

6. Quantitative Analysis

In the ordinary quantitative analysis, the element composition in an unknown sample is obtained under the assumption that the ratio of the peak height or area of each unknown element to that of the standard sample is taken as the 0-th order approximation for the analysis if an adequate normalization or a correction calculation is made. Therefore, the accurate calculation of the peak height or area is a primary step for obtaining the accurate quantitative analysis. In this report we compare the net peak areas calculated by the linear or the Shirley method. Fig. 5 shows the background subtracted spectrum by the linear method, and Table 1 shows the comparison of the relative areas(%) obtained by the linear and the Shirley background subtraction. The calculated result shows that the difference in the area is small (within 2%) but not negligible for the accurate quantitative analysis for AES or XPS with a high background. However, this difference is found to be negligibly small in EDX with a low background.

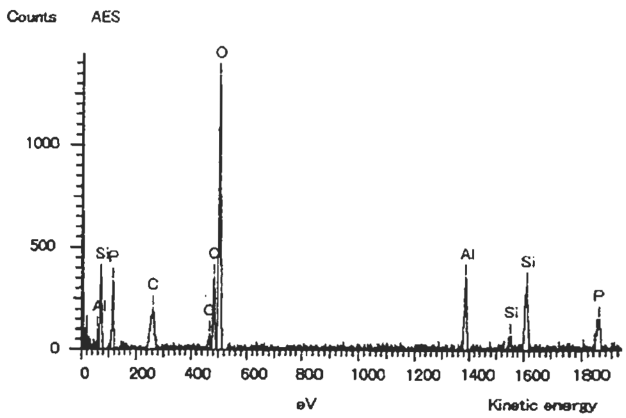

Fig. 5 Background subtracted spectrum for AES.

Element	Linear	Shirley	Difference
C	10.2	8.7	−1.5
O	43.2	43.7	+0.5
Al	13.7	14.0	+0.3
Si	19.8	21.9	+2.1
P	13.2	11.7	−1.5

Table 1 Comparison of the relative areas(%) obtained by the linear and the Shirley background subtraction.

7. Conclusions

In this report, the basic data processing techniques for the peak detection, qualitative and quantitative analyses with a spectrum obtained by surface analysis instruments are summarized. These techniques were proved to be reasonably satisfactory in both theory and practice.

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