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Technical Report

Practical Methods for Detecting Peaks in Auger Electron Spectroscopy and X-Ray Photoelectron Spectroscopy

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Three kinds of peak detecting algorithms for AES and XPS spectrum are proposed. These peak detecting methods are composed of three stages of algorithms: rough estimation of the background; direct calculation of the peak and background relation at the candidate peak; and application of the second derivative curve. This report provides concrete methods of finding peaks in a measured spectrum of surface analysis based on an empirical investigation of how to detect significant signals among faint ones. Algorithms and characteristics of the respective peak detecting methods are discussed.

1. Introduction

The presence of peaks in the spectrum obtained from the original data must first be determined as the primary source of information, when a qualitative or quantitative analysis is carried out for AES and XPS, especially when making a decision on the presence of elements.

Surface chemical analysts use many different methods to detect peaks in data, but as there may be no uniquely defined perfect method, analysts sometimes pick peaks visually. However, since scientists often rely on computers to perform basic analyses of data, scientists and instrument manufactures have developed their own peak detecting algorithms [1]. Their algorithms and techniques rely on straightforward methods for calculating the peak locations.

There are different ways to write algorithms to detect peaks, but their algorithms are not sufficiently clarified, nor do they always work for poorly resolved peaks. Since each method has relative merits, it is desirable for analysts to understand each algorithm and its performance in order to select the best or alternate method.

It is also important to track accurately and verify what has been done to the data. Data files processed by programs should leave a comprehensive audit trail to ensure traceability. To satisfy the strictest compliance standards, the appropriate audit trail should contain a complete description of the processing methods and equations applied to the data as well as program version.

This report provides concrete methods of finding peaks in a measured spectrum of surface analysis based on an empirical investigation of how to detect significant signals among faint ones. The purpose of this report is to give analysts a practical guide for finding peaks in a spectrum using their algorithms.

In the activity that relates to the international standardization in ISO TC201-SC3-WG4 (Surface Chemical Analysis-Data Management and Treatment- Peak Detection), three peak detecting methods have been proposed and discussed.

2. General considerations regarding peak detection

Described herein are basic data processing methods and specific aspects of detecting peaks such as peak detection criteria, the detection of poorly resolved peaks, small and broad peaks and overlapped peaks with valleys.

2.1. Peak detection criteria

In order to define peak detection criteria, it should be assumed that the data obtained with a pulse-counting detector will obey statistical theory based on the Poisson distribution. Then, empirical conditions for the detection criteria can be naturally defined, and concrete techniques for practical peak detection methods can be obtained.

"Peak detection criteria" is specifically referred to empirically determined criteria for detecting peaks in AES and XPS spectra, which are normally acquired without distortion due to instrument error, except for random noise.

Strictly speaking, the peak in question may have different background intensities on its lower and higher energy sides. In such a case, the presence of the peak should be decided by setting conditions on both sides of the peak independently. However, this makes it too complex to develop the argument further, so sometimes the peak is assumed to have a nearly flat or linear background on both sides, and it is further assumed that the peak can be decided by a single decision inequality.

3. Peak detection methods

The proposed peak detection methods are composed of three kinds of algorithms: for making a rough estimation of the background, for using the second derivative curve, and for directly calculating the peak and background relation at the candidate peak. The algorithms of these three methods are described in the following.

3.1. Peak detection using rough estimation of spectrum background

This method firstly assumes that the background curve of a spectrum is generally gentle and the total spectrum region containing peaks is much narrower than the region without peaks, 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, it can be approximately expanded by using the $2m+1$ points of data which cover the region with several times of the typical full width at half maximum of the peak,[*] w. The number of averaging points, $2m+1$, is selected so as to be equal to several times of the number of points in the typical full width at half maximum of the average peak of the spectrum.

The background b_i (i=1,T) (where, T is the total sampling points) then can be approximately written by using the given spectrum data y_i as follows:

$$b_i = \sum_{j=-m}^{m} h_j y_{i+j} \tag{1}$$

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 by using such expansion as follows [2]:

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

where $(Var)_{i+j}$ is the variance of y_{i+j} and $(Cov)_{[i+j],[j+l]}$ the covariance of y_{i+j} and y_{j+l}. If the random nature of the spectrum data y_i which obeys statistical theory based on the Poisson distribution is assumed,

$$(Var)_{i+j} = y_{i+j} \tag{3}$$

Further, each y_i is measured independently, and may have no correlation with each other, then:

$$(Cov)_{[i+j],[j+l]} = 0 \tag{4}$$

Then, the variance of b_i can be approximately expressed as

$$\sigma_{bi}{}^2 = \sum_{j=-m}^{m} h_j{}^2 y_{i+j} = \frac{1}{(2m+1)^2} \sum_{j=-m}^{m} y_{i+j} \tag{5}$$

If the variance of $n_i=y_i-b_i$ is defined as $\sigma_{ni}{}^2$, it can be estimated as follows:

$$\sigma_{ni}{}^2 = \sigma_{yi}{}^2 + \sigma_{bi}{}^2 = y_i + \frac{1}{(2m+1)^2} \sum_{j=-m}^{m} y_{i+j} \tag{6}$$

Therefore, the final inequality to judge a peak is given by using the critical value $k≈2$~3,

[*]The typical full width at half maximum of the average peak: Generally, spectra acquired with an instrument such as AES or XPS include peaks with certain range of FWHM. "The FWHM of the average peak" represents the approximate value for the FWHMs of such peaks. For example, it is 20 eV for AES and 10 eV for XPS, which may be allowed to adopt as default values.

$$n_i > k\sigma_{ni} = k\sqrt{y_i + \frac{1}{(2m+1)^2}\sum_{j=-m}^{m} y_{i+j}} \quad (7)$$

or, in a more familiar expression,

$$y_i > b_i + k\sigma_{ni} \quad (8)$$

where $b_i + k\sigma_{ni}$ defined as the noise threshold curve. The local maximum y_i satisfying the inequality Eq. (8) is regarded as a peak (see Fig. 1.).

Furthermore, in order to apply this procedure more effectively for the practical situations, some exceptional cases should be taken into consideration. In one of such situations, there is the case that some especially broad peaks in the spectrum do not satisfy inequality Eq. (8).

In order to cope with these situations, a peak, which satisfies the following inequality, is included if its S_i^* is greater than a certain value S_{i0}^{**}.

$$S_i > S_{i0} \quad (9)$$

The approximate value of S_{i0} is roughly estimated by assuming it as an ideal triangle peak with the typical full width w at half maximum of the peak and height $k\sigma_{ni}$ (noise threshold curve), then its peak area S would be, $1/2\times2\times w\times k\sigma_{ni}=wk\sigma_{ni}$.

$$S_{i0} = k\sigma_{ni} w \quad (10)$$

In fact, if the peak area Si is greater than the value above, the peak is found to be real one in most of the cases [3].

For poorly resolved peaks with deep valleys, the following data processing is effective. If the spectrum has plural peaks above noise threshold curve $k\sigma_{ni}$ and valleys that do not cross the noise threshold curve, and if valley depth D^{***} of the minor local maximum in the spectra exceeds the noise fluctuation $k\sigma_{ni}$, the peaks are regarded as real.

$$|D| > k\sigma_{ni} \quad (11)$$

By adding such exceptional cases, this peak-detection method becomes effective in the actual spectrum processing.

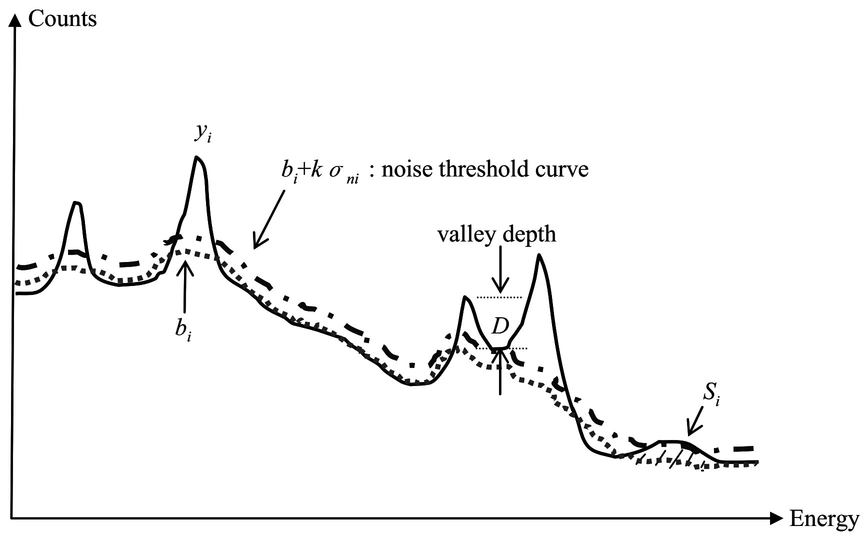

Fig. 1. Schematic diagram of y_i, b_i and $b_i+k\sigma_{ni}$.

$^*S_i$: The software evaluates the (i-th) peak area by summing the difference from the measured spectrum value to the background value at every successive position while the difference is positive.

$^{**}S_{i0}$: This is obtained as the area of the triangle (typical noise peak) by multiplication of typical FWHM and $k\sigma_{ni}$.

***Valley depth, D: The software evaluates the valley depth by searching a local maximum that exceeds the deviation of the noise height and, just after finding the local maximum, a local minimum that exceeds the deviation of the noise height, and calculating the difference between the local maximum and the local minimum.

3.2. Peak detection using threshold curve of second derivative

This method has the same effect as subtracting the background from the spectrum, by making use of the second derivatives. And because it has no arbitrariness in the background subtracting procedure, it may be a relatively convenient algorithm when we use it with the aid of computers.

By making use of the moving polynomial approximation procedure (Savitzky-Golay method), it is possible to calculate the second derivative spectrum d_i from the original spectrum y_i as follows:

$$d_i = \sum_{j=-n}^{n} g_j y_{i+j} \qquad (12)$$

where, g_j ($j = -n, n$) is the Savitzky-Golay coefficients for the second derivative, and if $2n$+1 points of data cover roughly the half width of the typical peak, the obtained second derivative will faithfully represent the true second derivative curve. If it is expressed as mentioned above, the variance σ_i^2 of d_i can be obtained as follows:

$$\sigma_i^2 = \sum_{j=-n}^{n} g_j^2 (Var)_{i+j} + \sum_{j=-n}^{n}\sum_{l\neq j}^{n} g_j g_l (Cov)_{[i+j],[i+j]} \qquad (13)$$

where $(Var)_{i+j}$ is the variance of y_{i+j} and $(Cov)_{[i+j],[j+l]}$ the covariance of y_{i+j} and y_{j+l}. Again, if we assume the random nature of the spectrum data y_i which obeys statistical theory based on the Poisson distribution, then:

$$(Var)_{i+j} = y_{i+j} \qquad (14)$$

Further, each y_i is measured independently, and may have no correlation with each other, then:

$$(Cov)_{[i+j],[j+l]} = 0 \qquad (15)$$

Thus, the variance σ_i^2 of d_i can be approximately calculated as follows:

$$\sigma_i^2 = \sum_{j=-n}^{n} g_j^2 y_{i+j} \qquad (16)$$

As the peak in the spectrum corresponds to the local minimum of the spectrum, we judge the peak is real one if the local negative minimum $d_{\min}$ is less than (in absolute values, greater than) its noise fluctuation.

Therefore, for the peak judge inequality, if the following inequality Eq. (17) is satisfied, we admit the peak is detected at the position that gives $d_{\min}$ in the second derivative if the following inequality is satisfied [3,4],

$$d_{\min} < k\sigma_i \qquad (17)$$

where $k\sigma_i$ defined as the noise threshold curve.

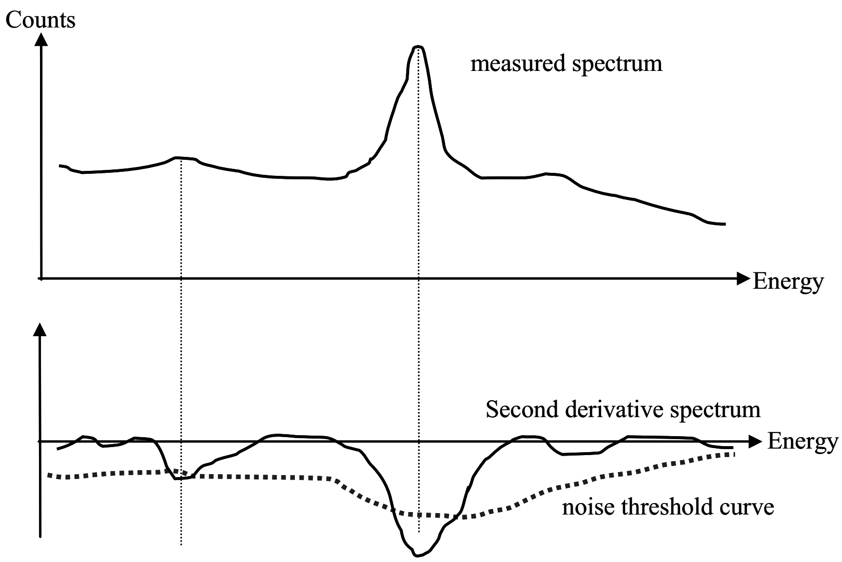

Fig. 2. Schematic diagram of a peak position, second derivative curve and threshold noise curve.

3.3. Peak detection by directly calculating peak and background relations at the candidate peaks

In this method, the candidate peaks are detected by the second derivative treatment and judged by comparison with criteria.

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

(1) Calculate the second derivative curve (e.g. by using Savitzky-Golay method [4]) and calculates the standard deviation (σ_i) for the second derivative curve.

(2) Pick up the candidate peak positions satisfying the local minimum (nagative value) of the second derivative curve is negative.

(3) Let p be a candidate peak position, and w be the typical full width at half maximum of the peak* in the original spectrum, where w is usually given in the peak detection condition (see Fig. 3.). If there exists a positive local maximum at $x=p_1$ in the second derivative spectral range, $p\text{-}3w \le x < p$ in the nearest candidate peak (if does not exist, the position, $p_1=p\text{-}3w$ is regarded as the position), the position, p_1 is regarded as a midway one to the left-side background, and furthermore if there exists a local minimum in the smoothed spectrum or a zero cross position in the second derivative spectrum at $x=q_1$ in the spectral range, $p_1\text{-}2w \le x < p_1$ in the nearest candidate peak (if does not exist, the position, $q_1=p_1\text{-}2w$ is regarded as the position), the distance, $l_1=p\text{-}q_1$ corresponds to the left-side background position $p\text{-}l_1$ with intensity B_1.

(4) Likewise, If there exists a positive local maximum at x in the second derivative spectral range, $p<x\le p+3w$ in the nearest candidate peak (if does not exist, the position, $p_2=p+3w$ is regarded as the position), the position, $x=p_2$ is regarded as a midway one to the right-side background, and furthermore if there exists a local minimum peak position in the smoothed spectrum or a zero cross position in the second derivative spectrum in the spectral range, $p_2\le x<p_2+2w$ in the nearest candidate peak (if does not exist, the position, $q_2=p_2+2w$ is regarded as the position), the distance, $l_2=q_2\text{-}p$ corresponds to the right-side background position $p+l_2$ with intensity B_2.

(5) 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

$$B = (B_1 l_2 + B_2 l_1)/(l_1 + l_2) \tag{18}$$

The background intensity, B, at the candidate peak position is estimated by adding the fractional background intensities from both sides of the peak, B_1 and B_2, which are inversely proportional to the distances

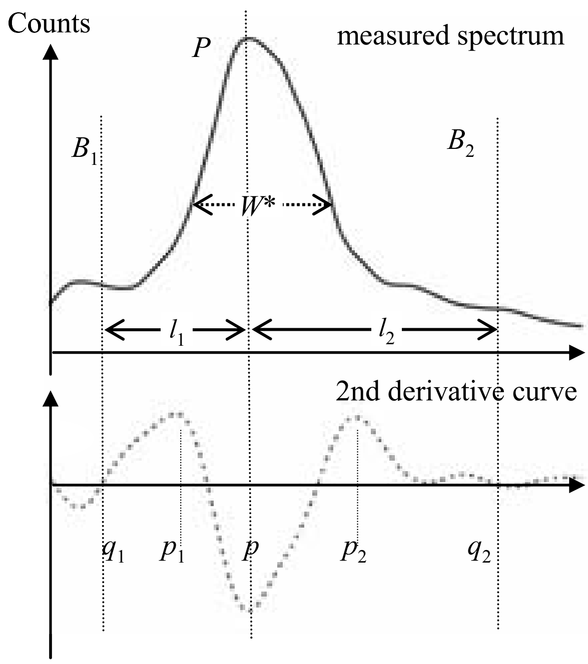

Fig. 3. Schematic diagram of a peak position and its background at both sides of the peak.

*The typical full width at half maximum of the average peak : refer to 3.1.

from the peak to both sides of background positions l_1 and l_2.

Let P denote the peak intensity with the background and N the net peak intensity, then, N=P-B, and the variance σ_N^2 of N is calculated as follows [5]:

$$\sigma_N^2 = \sigma_p^2 + \sigma_B^2, \tag{19}$$

where

$$\sigma_p^2 = P, \quad \sigma_{B1}^2 = B_1, \quad \sigma_{B2}^2 = B_2, \tag{20}$$

and

$$\sigma_B^2 = [l_2/(l_1+l_2)]^2 \sigma_{B1}^2 + [l_1/(l_1+l_2)]^2 \sigma_{B2}^2, \tag{21}$$

then, σ_N^2 is calculated as follows:

$$\sigma_N^2 = P + \left(B_1 l_2^2 + B_2 l_1^2\right)/\left(l_1+l_2\right)^2 \tag{22}$$

Therefore, the peak decision condition is given as follows:

$$N > k\sigma_N \tag{23}$$

If the second derivative curve does not cross the horizontal axis within a distance of 3 times the peak width (full width at half maximum of a typical peak) from the candidate peak position on both sides of the peak, we accept the position with a distance of 3 times the peak width from the candidate peak position as a background position for the peak.

4. Some practical examples

4.1. General

Some practical examples applied to the typical spectra of AES and XPS using codes written for computing are shown for the three peak detection methods. Fig. 4. Figures 5 and 6 show AES spectra, Figs. 7-9 show XPS spectra. Each processing condition is shown below, where *T*, *Bsmp*, *Smp*, *Step* and *Typw* stand for the total sampling points, smoothing points of background, smoothing points of spectrum, sampling step width and typical peak width of the spectrum, respectively, and *k* is the critical value shown in each peak detection formula.

4.2. Processing conditions

4.2.1. AES spectrum

T=2001, *Step*=1 eV, *Typw*=20 eV
Figure 4: *Bsmp*=31, *k*=2.5
Figure 5: *Smp*=13, *k* =1.4
Figure 6: *Smp*=13, *k* = 2.5

4.2.2. XPS spectrum

T=1001, *Step*=1 eV, *Typw*=10 eV
Figure7: *Bsmp*=31, *k*=3
Figure 8: *Smp*=7, *k*=2.5
Figure 9: *Smp*=11, *k*=3

5. Summary

5.1. Relative merits of each method

Proposed peak detection methods for a spectrum are not fully perfect but if the parameters such as *Smp*, *Bsmp*, *Step* and *Typw* for the detecting algorithms are given properly in automatic computing, finely good results are obtained for practical uses as shown in Figs.4-9. Summarized relative merits of each method are shown in Table 1.

6. Acknowledgement

The author would like to thank Dr. Yoshitaka Nagatsuka for developing these peak detection algorithms. Local members of TC201SC3WG4 in Japan are also acknowledged for their developing codes for computing and useful advice and fruitful discussion.

7. References

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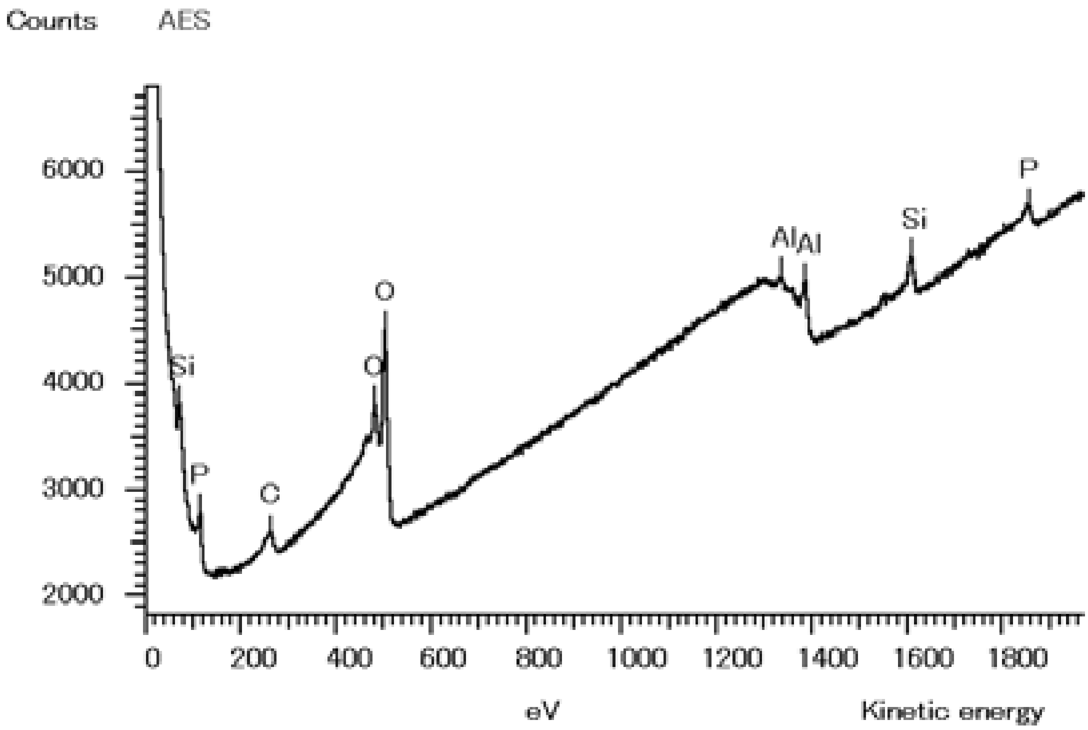
Table 1 Relative merits of each method.

Kind of peak	Peak detection method	Results
(1) Single small peak	1. Background estimation	Almost good
	2. 2nd derivative	Sometimes neglects broad peaks
	3. Peak and Background relations	Sometimes neglects broad peaks
(2) Single large peak	1. Background estimation	Good
	2. 2nd derivative	Sometimes finds spurious peaks at peak base
	3. Peak and Background relations	Good
(3) Grouped small peaks	1. Background estimation	Sometimes neglects small peaks
	2. 2nd derivative	Sometimes neglects broad peaks
	3. Peak and Background relations	Sometimes neglects small peaks
(4) Shoulder peak	1. Background estimation	Not appropriate
	2. 2nd derivative	Sometimes neglects shoulder peak
	3. Peak and Background relations	Sometimes neglects shoulder peak

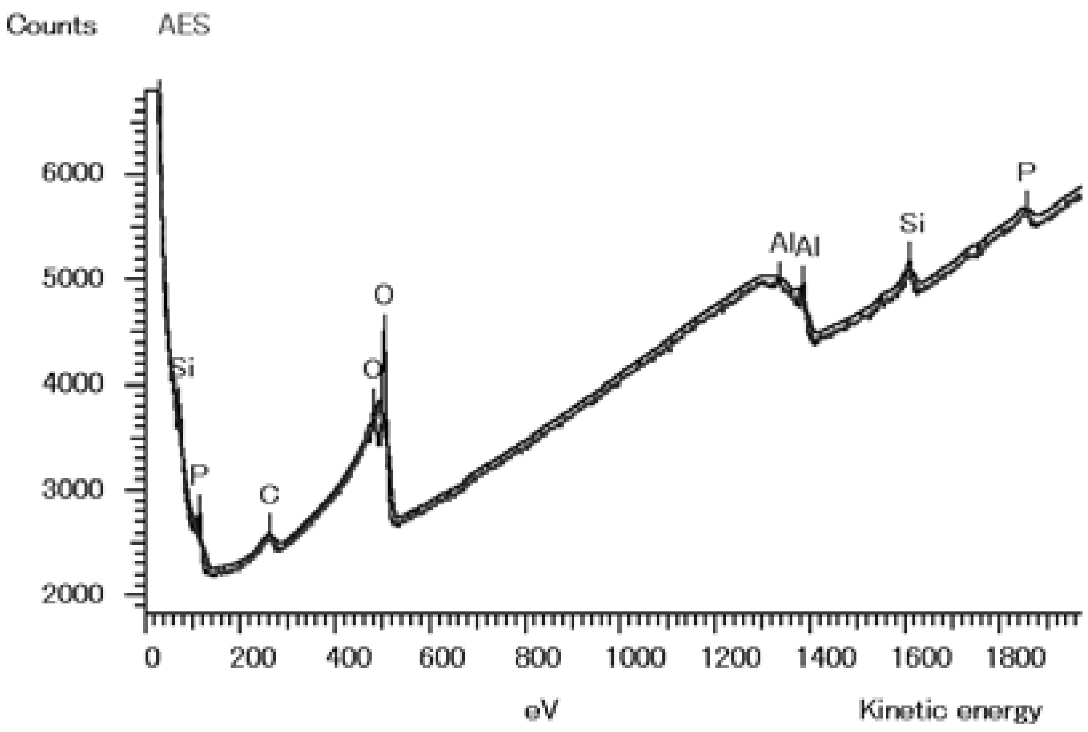
Notes

Names of Peak detection method in Table1 are short for followings.

1. Background estimation: Peak Detection Using Rough Estimation of Spectrum Background in 3.1.
2. 2nd derivative: Peak Detection Using Threshold Curve of Second Derivative in 3.2.
3. Peak and Background relations: Peak Detection by Directly Calculating Peak and Background Relations at the Candidate Peaks in 3.3.

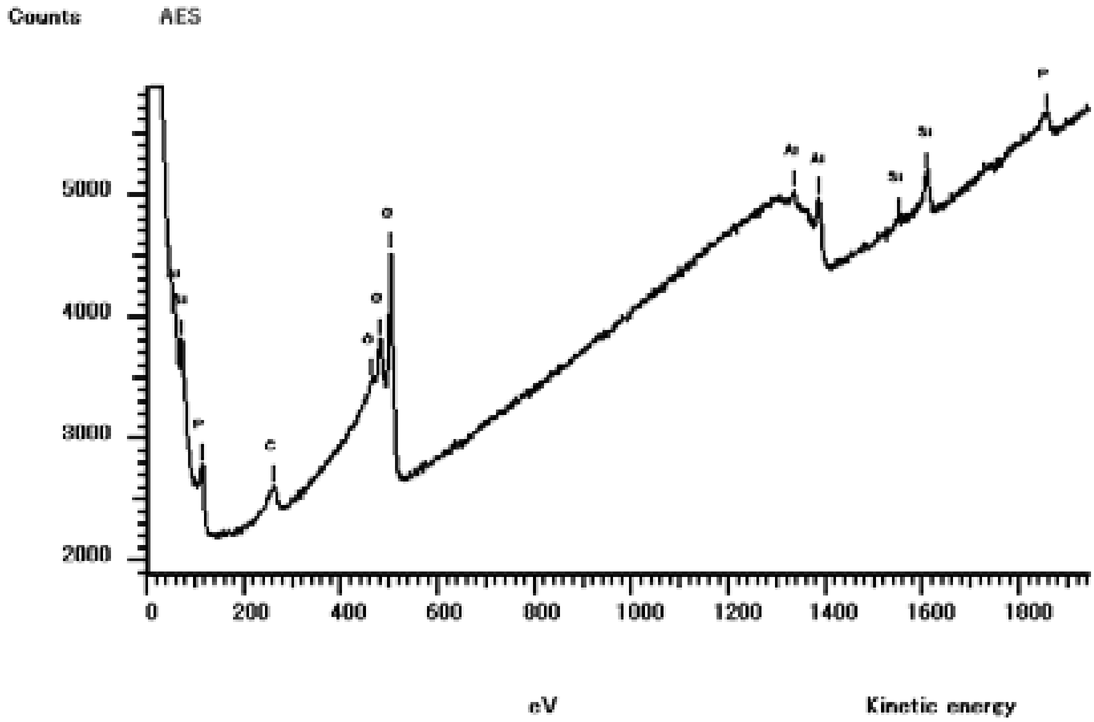


(a)

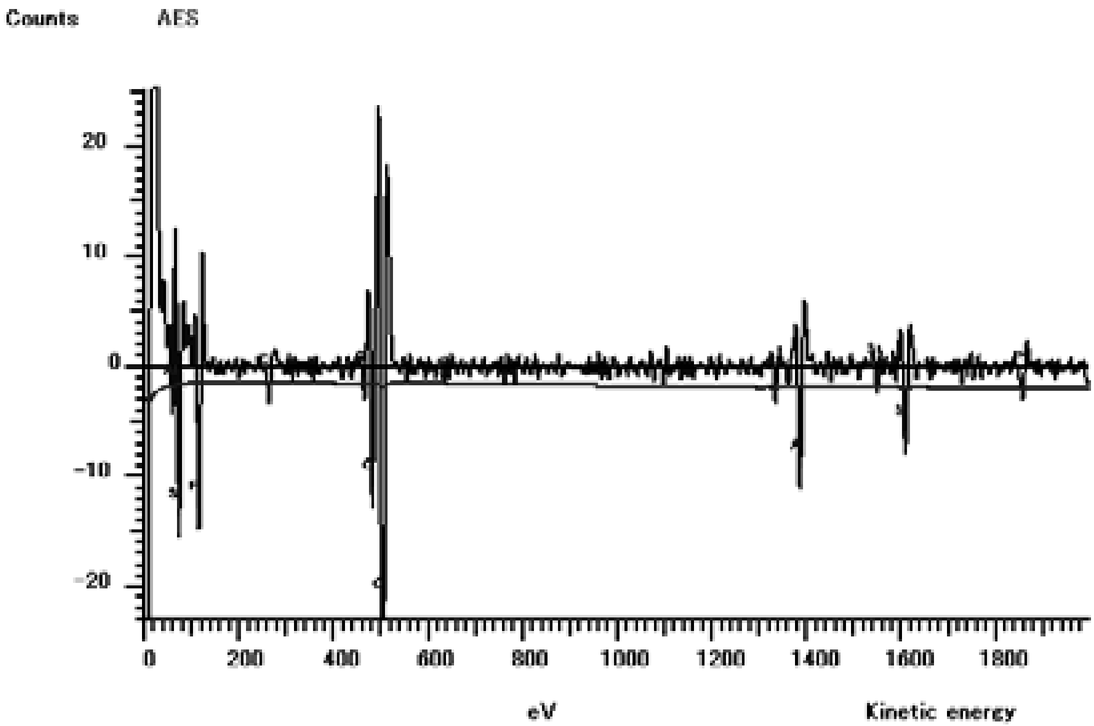


(b)

Fig. 4. (a) Example of AES peak detection using the method shown in 3.1. (b) Noise threshold curve of the above peak detection.

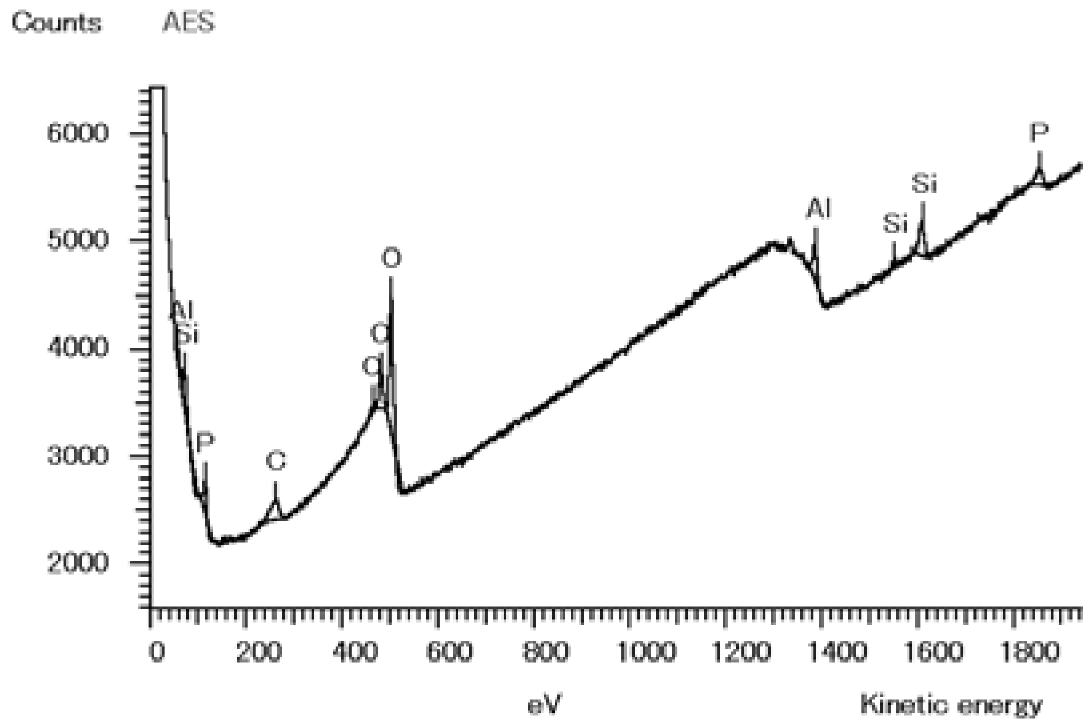


(a)

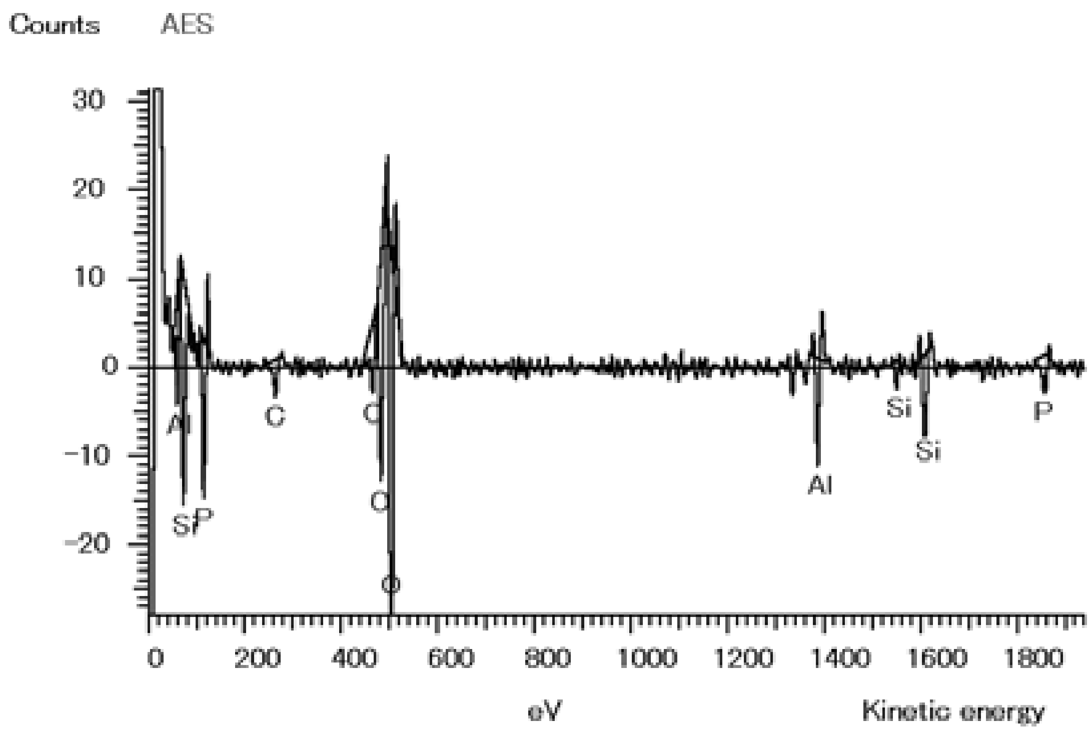


(b)

Fig. 5. (a) Example of AES peak detection using the method shown in 3.2. (b) Second derivative curve of the above peak detection.

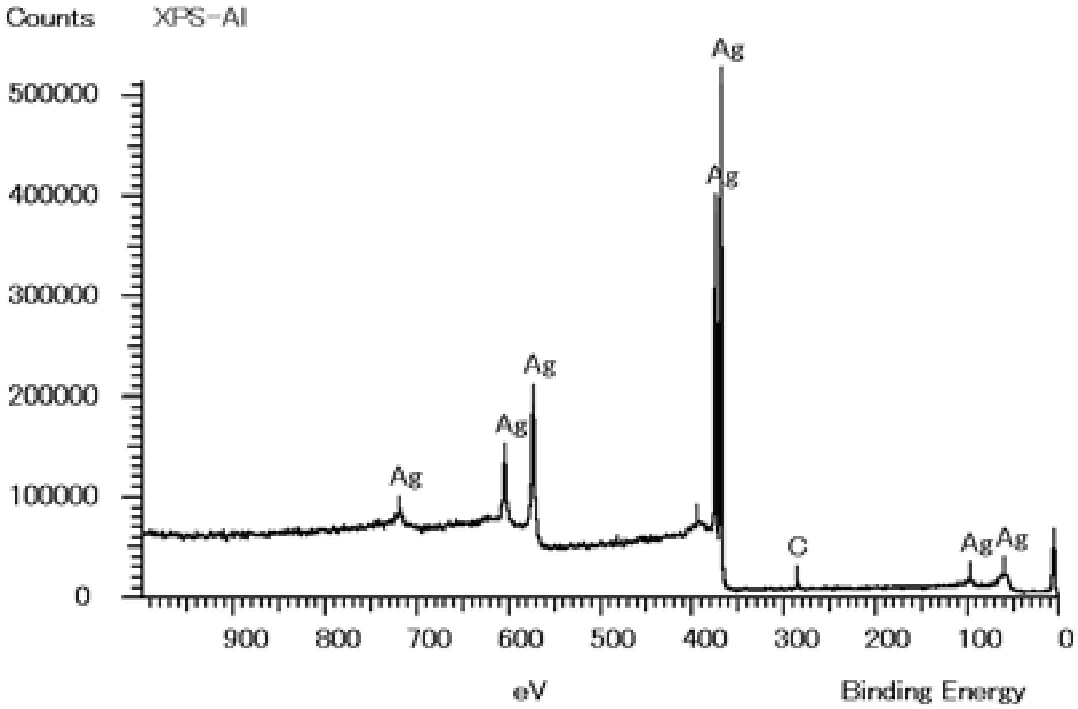


(a)

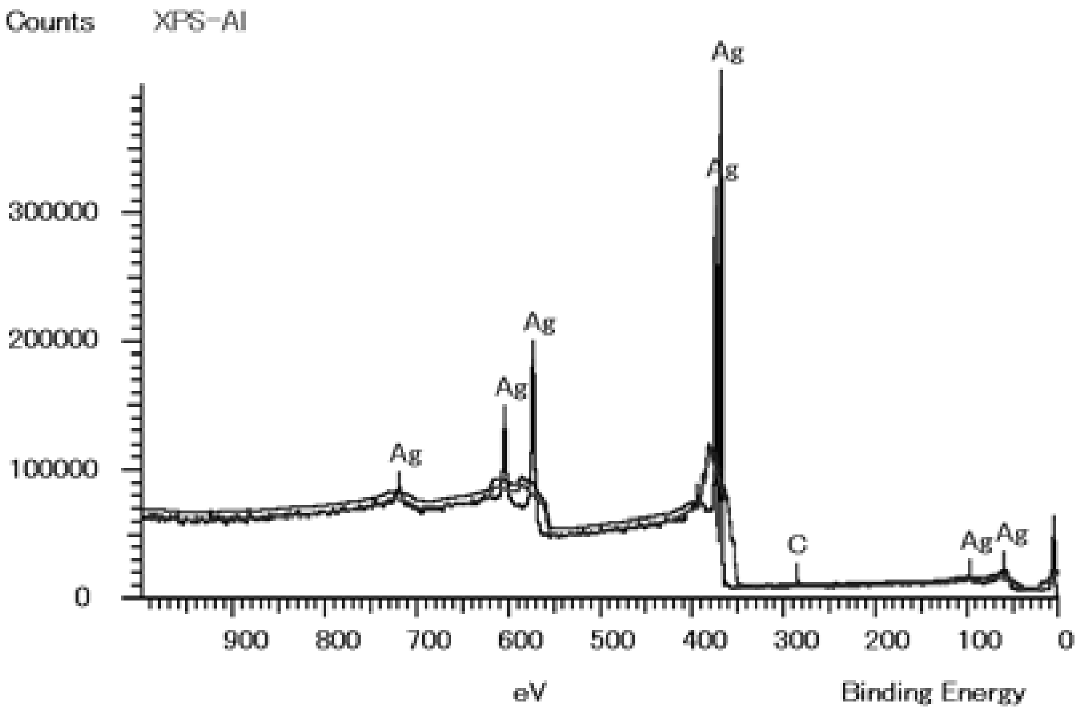


(b)

Fig. 6. (a) Example of AES peak detection using the method shown in 3.3. (b) Second derivative curve of the above peak detection.

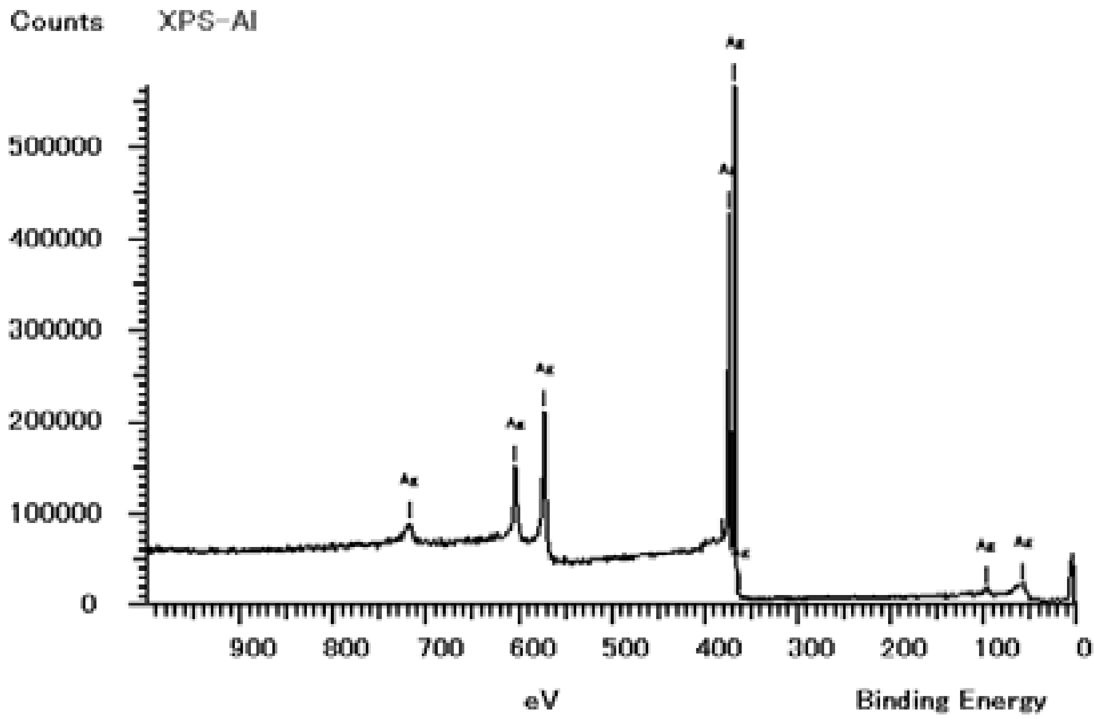


(a)

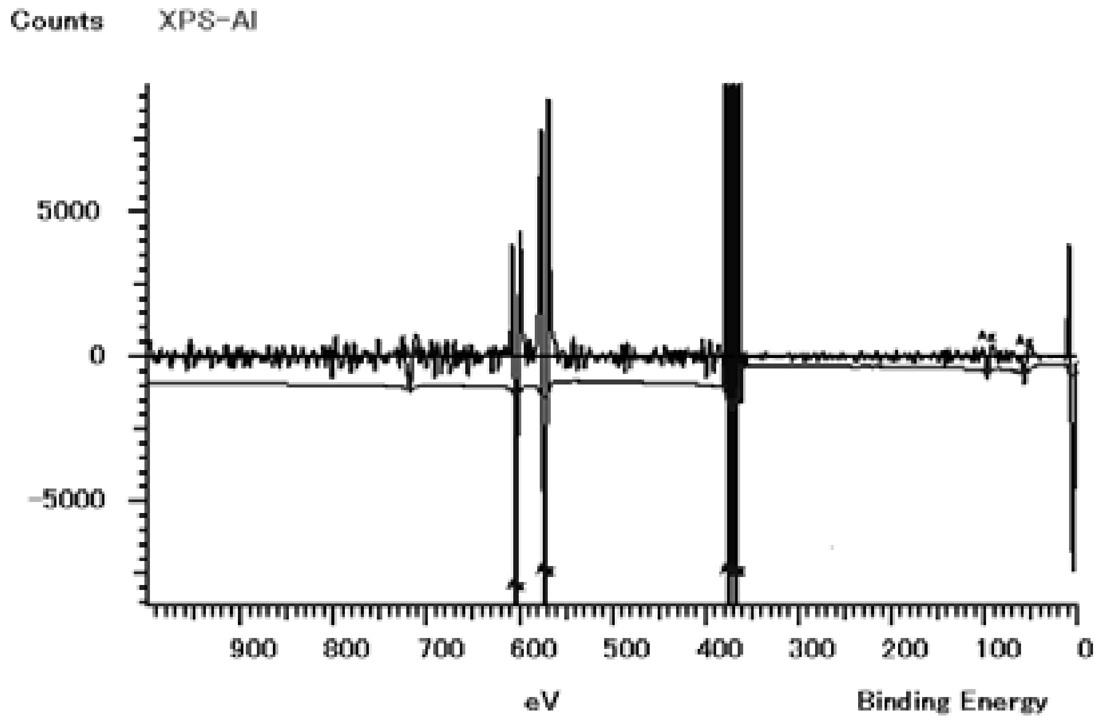


(b)

Fig. 7. (a) Example of XPS peak detection using the method shown in 3.1. (b) Noise threshold curve of the above peak detection.

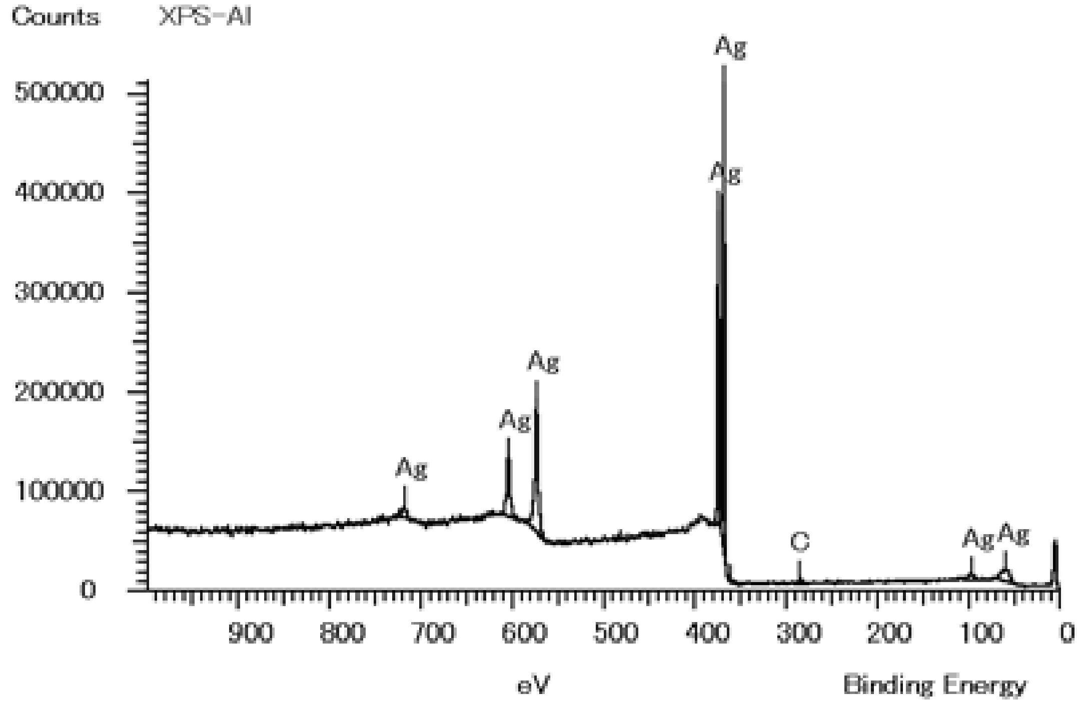


(a)

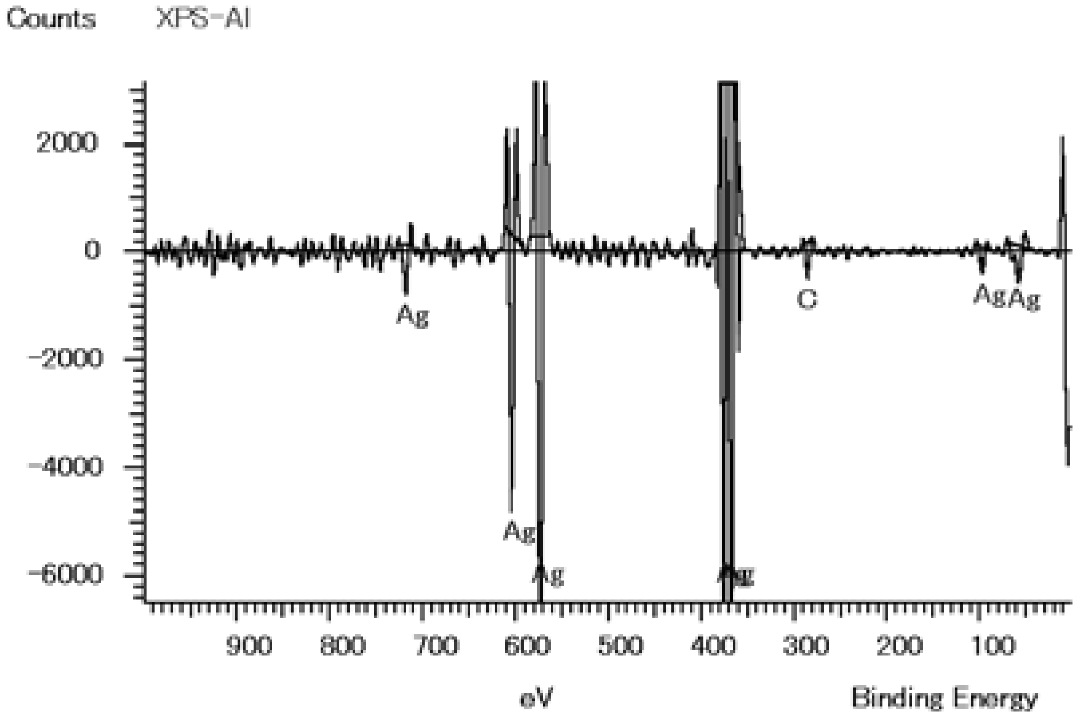


(b)

Fig. 8. (a) Example of XPS peak detection using the method shown in 3.2.(b) Second derivative curve of the above peak detection.



(a)



(b)

Fig. 9. (a) Example of XPS peak detection using the method shown in 3.3. (b) Second derivative curve of the above peak detection.

査読コメント

査読者 1．吉原一紘（アルバック・ファイ）

ピーク位置の判定に関する汎用性のあるアルゴリズムの提案は実用上重要な課題ですので，掲載に値すると思いますが，いくつか初歩的なことで不明な点がありましたので，お教え頂ければ幸いです．

［査読者 1-1］

ピークディテクションの第 1 の方法としてあげられているスペクトルのバックグラウンドを見積もる方法ですが，(1)式で記述されているバックグラウンドの定義はあるデータ点（i）のバックグラウンド b_i はそのデー点の周りの 2m+1 点の平均と見なすということのように思えます．もしそうならば，y_{i+j} の variance は以下のようになります．

$$\frac{\sum_{j=-m}^{m}\left(y_{i+j}-b_i\right)^2}{2m}$$

この式は直ちには(3)式にはならないような気がします．

［著者］

AES や XPS の計測は電子 1 個 1 個を計測しますから計数値は整数となります．一方，分光法や液体クロマトグラフ装置やガスクロマトグラフ装置からの出力はアナログ扱いとなり測定値は実数です．後者の測定値はガウス分布（正規分布）となりますが，前者の計数値は Poisson 分布に従います．Poisson 分布に従う計数値の標準偏差は計数値（期待値）の平方根と表され，また分散（Variance）は標準偏差の二乗ですから計数値（期待値）そのものとなります．また期待値は複数測定値の平均値で表されます．従いまして(1)式の BG 値の分散は，係数の h_j が 2 乗となるもの，基本的には計数値そのもので表します．逆に言えば分散（Variance）が上式のように書けるというのは実は，その統計事象がランダムで正規分布に従うことを暗黙に仮定しています．電子計測の場合には，計測値の分布は正規分布ではなく，厳密には Poisson 分布であり，分散の 2 乗が平均値になるという事実だけを用いていますので，(3)式の方が上式よりも厳密に成り立つ式になります．

［査読者 1-2］

また，ここで covariance に関する議論がありますが，結局は covariance=0 としているので気にする必要は無いのかもしれませんが，同一スペクトル上でのデータ点の間の covariance という意味が分かりません．なお，m の値はどのように設定するのでしょうか．

［著者］

Covariance とは単純にデータ点間の相関という意味です．ランダム実験におけるランダムデータの誤差が Variance と Covariance で書けることは，References で引用しております Peter Gans, “*Data Fitting in the Chemical Sciences*” Wiley, (1992)に書かれています．全くのランダムな事象ではない限り厳密には相関は 0 にはなりませんが，少なくともデータのノイズ成分には相関がないことは明らかですので，Variance に比べて，Covariance の寄与は少ないと仮定して 0 としています．逆に言えば，この寄与が 0 にならないと，この問題を扱う手立てがなくなってしまいます．しかし，この定式化では共分散が評価できないからそれを 0 にするというのも乱暴な話ですので，データの取得方法が独立である，つまり，Further, each y_i is measured independently, and may have no correlation with each other, then:と修正しました．

また，m の値の決め方については，2m+1 が取り得る幅を AES や XPS で得られる標準的な半値幅の数倍となるように決めます．本文中に記述します．

［査読者 1-3］

ピークディテクションの第 3 の方法としてあげられている 2 次微分を用いる方法ですが，この方法は南茂夫先生著の「科学計測のための波形データ処理」に記述があります．南先生は「実際の観測波形では無数の極大値が発生するので，平滑化微分の点数の選択が重要であり，雑音の分散に応じてその範囲を変化させる必要がある.」と指摘しています．ここでは p-3w<x<p の範囲で極値を探すという記述がありますが，南先生が指摘されるように，その間に発生する無数の local maximum/minimum をどのように排除するのかを記述していただければと思います．

［著者］

2 次微分に閾値を設定して判定しています．ただし，実際には，再度 **Peak** と **Background** の比を使ってピークの存在を再確認しますので，閾値の係数は第 2 の方法としてあげている 2 次微分法に比べ 1/3 に小さくし，出来うる限りピークを拾う様にしています．

一方，微分点数を変化させることも考えられますが，微分点数を小さく（または大きく）すると，それにつれてノイズの(平均)分散曲線も変わります．

従って，最適には微分点数がそのピークの半値幅程度になるように選ぶことになります.

［査読者 **1-4**］

ピークディテクションの第 2 の方法としてあげられている 2 次微分に閾値を設定して判定する方法は,［査読者 1-3］で述べた望まない極値を排除する方法になるのでしょうか.

［著者］

上記［査読者 1-3］に対する見解と同じです.

［査読者 **1-5**］

(17)式の g_i は Savitzky-Golay の係数ですから d_i は微分値です．第 1 の方法の場合は b_i が平均値でしたから，variance の意味は理解できましたが，variance が平均からのずれを示す値だとすると，y_{i+j} の variance と d_i の variance は(21)式に示されているようには直接には結びつかないように思えます.

［著者］

微分すると background は消えますので d_i の項のみとなります．その後の統計的な処理に対する考え方は, Poisson 分布に従う計数値の取り扱いになりますので,［査読者 1-1］に対する説明と同じになります.

［査読者 **1-6**］

「バックグラウンド」について，(3)式は，計数値 Nの誤差が $\sqrt{N}$ になることを示しており，この式自体にはもちろん問題はありません．ただし，この論文では計数値の回りの 2m+1 個の平均点をとったものをバックグラウンドとしています．ある計数値の回りの 2m+1 個のデータの平均をとると言うことは, 2m+1 個のエネルギーの違った箇所でのデータを足しあわせてその平均をとることですので，得られたバックグラウンドとしての値の誤差には各データ点のポアソン分布に起因する計数誤差だけではなく，測定したエネルギー値の誤差に起因する計数値の誤差も含まれると思われます．variance を(3)式で取り扱うためには,「あるデータ点の周りの 2m+1 個のデータ点の平均をそのデータ点のバックグラウンドとする」ということと「期待値は複数測定値の平均で表される」ということを結びつける説明をしていただくことが必要ではないでしょうか.

［著者］

ここでいうバックグラウンドとは本当のバックグラウンドではなく，ピークを検出するためだけの仮のバックグランドですから，大雑把で良いと考えています．ピークが適当に潰れてくれれば十分目的を果すことができます．また，測定したエネルギー値の誤差に起因する計数値の誤差も含まれることは確かにあり得ますが，ここでは単純にカウントの計測値にのみ起因する誤差によってピークの有無を判断することを考えています．エネルギー値の誤差に起因する計数値の誤差を考えても，その寄与はカウントの計測値にのみ起因する誤差に比べてかなり小さいと思われます.

一方，ご指摘の様に，バックグラウンドなどの計測値がポワソン分布に従う場合の取り扱い方の特徴を記述した方が良いと思われますので，(1)式の後に追記しました.

［査読者 **1-7**］

Fig. 1 について，私の方で作図をしてみますと Fig. 1 のようにはなりません．N_i の XPS データ（1 eV ステップで取得）を使って(1)式に基づいて，m=15 の場合について作図してみました．下図（Fig. Q&A-1）をご参照ください．（論文では XPS のピークの標準 FWHM を 10 V とし，その数倍を 2m+1 点とすると記述されていますので，m=15 としました.）バックグラウンドがピーク内に入り込んでいる場合もあり, Fig. 1 とはかなり異なった挙動の図が得られています.

また，大きいピークの近傍では，ピークに引きずられバックグラウンドがかなり上昇しています．したがって，ピークの近傍に出現する小さなピークはバックグラウンドよりも小さくなり，判定されません．また，このバックグラウンドに(7)式で定義される分散を重ねますと（ここでは(7)式の k の値は 3 としています），下図（Fig. Q&A-2）が得られます.（分散の影響が小さいため一部を拡大しました．バックグラウンドに標準偏差を加えた値を紫色の線で書きましたが，ほぼ重なってしまいました.）このスペクトルに固有な事象かもしれませんが，標準偏差を足してもバックグラウンドの位置はほとんど変わらず, Fig. 1 のような分散の影響は現れませんでした．なお, 上図からは, 2 連のピークの「valley」の上にバックグラウンドが入り込み, Fig. 1 に示される 2 連ピークの場合とはかなり挙動が異なっています.

この曲線を通常の意味でのバックグラウンドと見なすことは少し無理があるのではないでしょうか.
本論文では「バックグラウンド」の定義は，3.1.節に記述してありますが,［査読者 1-6］の質問に対する

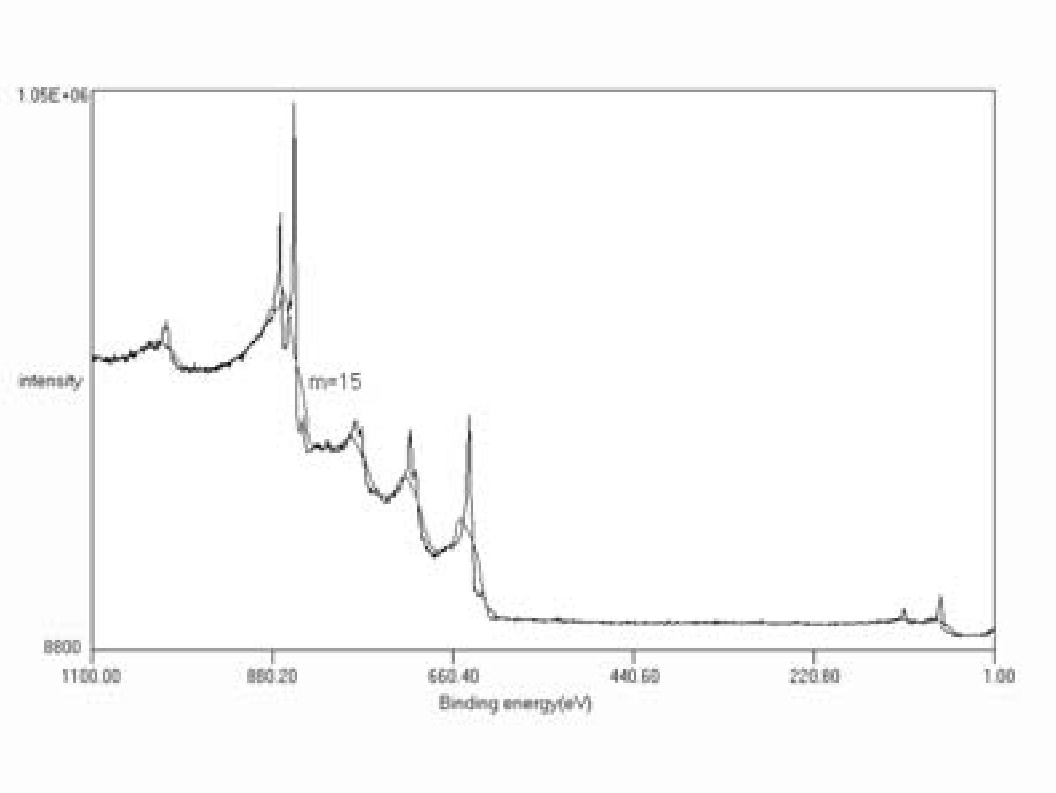


Fig. Q&A-1.

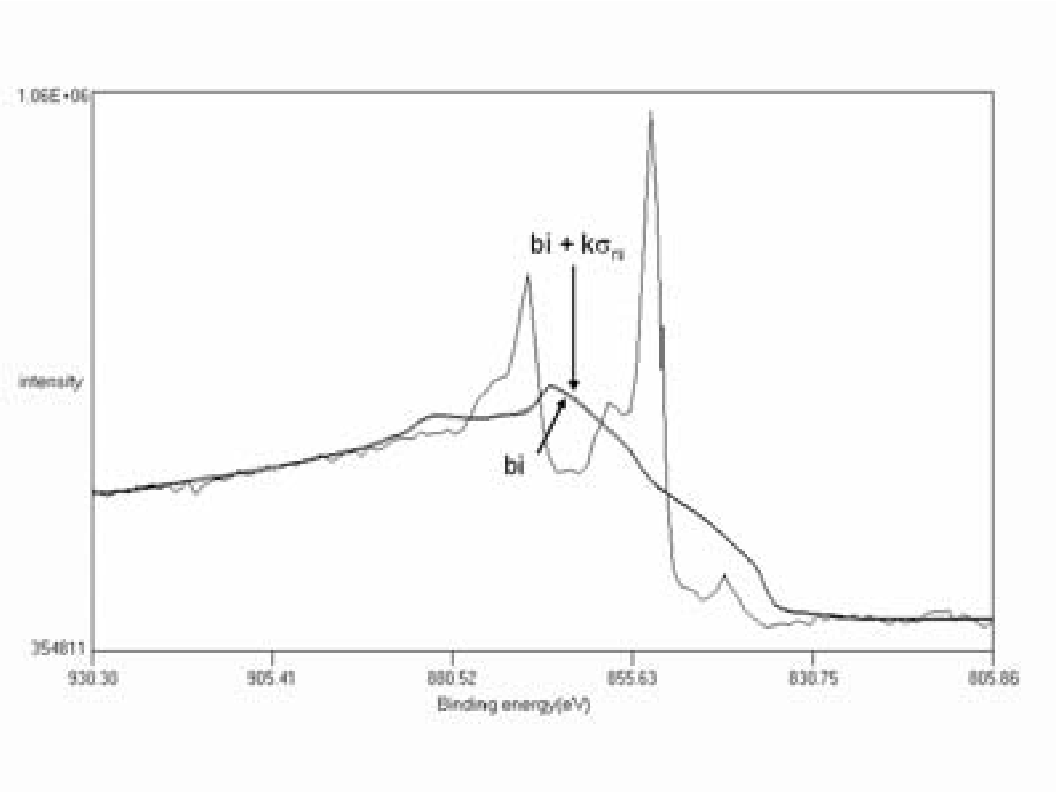


Fig. Q&A-2.

ご説明も含め，定義内容を少し加筆していただければ理解が進むのではないかと思います.

［著者］

本アルゴリズムをプログラム作成により再現戴き有り難うございます．アルゴリズム通りのバックグランド表示となっていますので，アルゴリズムの検証になっています．Fig. 1 の作図イメージが実際と異なる件ですが，アルゴリズムを理解していただくために誇張して描画しております．誇張しすぎない様に少し修正しました．実際の描画は Fig. 4(b), Fig. 7(b)で具体的に表示されています．確かに $b_i+k\sigma$は b_i より少し大きく表示されています．カウント数の高い領域では閾値線はバックグラウンドより更に上になると思われます．また計数値の大きさでバックグラウンドから離れる程度が異なってきます.

また 2 つのピークの谷底付近の閾値線の挙動ですが，ご呈示戴いた 2 つのピークは分離が良く，谷底がバックグランド近くまで落ち込んでいますので，閾値線は図示された位置にくると思われます．分離が悪い場合ですと Fig. 1 の様になることが期待されます.

査読者 2．城昌利（AIST）

［査読者 **2-1**］

It is more convenient to remind the readers that Eqs. (3) and (19) are the direct conclusions from the property of Poisson distribution.

［著者］

Next phrase, "which obeys statistical theory based on the Poisson distribution" is inserted after the phrase, "If the random nature of the spectrum data y_i".

［査読者 **2-2**］

In 3.2., the authors define the p_1 and p_2 as the points at the second derivative's local maxima. Are they more suitable than the zero-cross points, the inflection points?

［著者］

The p_1 and p_2 as the points at the second derivative's local maxima correspond to a flat position of background on both sides of a peak or flat point of valley between peaks. As red dotted line in Fig. 3 is distorted, it is modified a little to appropriate shape. It seemed hard correction for author to modify the second derivative curve perfectly this time.

［査読者 **2-3**］

In 3.1., I don't understand why they don't use the width w deduced in 3.2. for examining S. Obviously $w=(p_2-p_1)/2$, or (distance between inflection points) seems to be a better estimate for FWHM.

［著者］

The use of the typical full width at half maximum of the average peak as a default values is the feature of these three peak detection methods. For example, 20 eV for AES and rather big figure, 10 eV, for XPS are allowed to adopt as default values. As it is difficult to know any full width at half maximum or to calculate it before detecting peak, a default value is adopted in these three algorithms. Although the use the full width at half maximum deduced in 3.3. become possible only after detecting peaks or detecting candidate peaks, it is impossible to use the values before detecting peaks.

［査読者 **2-4**］

In addition to comment ［査読者 2-3］, it seems better to unify these three methods to give a best one. Is there a special reason to leave them separately? At least when the authors write codes, they should do so.

［著者］

Unfortunately the combination of these three methods constitutes an infringement of the patents.

［査読者 **2-5**］

As long as one needs to supply values such as *Smp*, *Bsmp*, *Step*, and to check the appropriateness of the result, there is not much practical difference between the present method and such conventional visual inspections by human eyes. Do you think if it is possible, in the future, to write a complete and automatic code that works without human aid, which is the ultimate purpose of this paper?

［著者］

It is hard to find a proper resolution of this comment. Some answer to this comment is given in "1.Introduction". As far as there may be no perfect method, analysts should find the best way by checking the performance of peak detecting method interactively with computer.

［査読者 **2-6**］

3 つの方法が特許のために統合できないとのことですが（［査読者 2-4］参照），それなら該当する特許を引用してください. この論文を読むと, 誰でも，統合するのが一番よいと気づくと思いますが，それができないのでは，発表する意味が何なのかわからず小生は困惑しました．特許が絡むとすると，これらを利用することも躊躇されます．もちろん，これらを利用した製品を売ってはいけないということで，読者が研究用としてこれを発展させるのは自由と解釈できますが，それでよいですか．権利が絡むのなら，このあたり，明確に書いておく必要があると思います.

［著者］

関連特許について引用しました．特許に関する注意事項まで記述しなくとも，その意味は常識的に言外に読み取って戴くことで十分と思われます．また本発表の目的は 3 種のアルゴリズムを個別に紹介することにあります．これらの手法のそれぞれの組み合わせ方も考えられますし，読者が組み合わせて使用することも可能ですが，それは次の段階のプロセスと思われます.

［査読者 **2-7**］

［査読者 2-3］の回答について, w は一度ピークを検出した後でないと，わからないから，検出には使えないとの回答は納得しかねるものがあります．どの方法も，フィルターをかけて得た量と元の量を比較する，という，複数の操作からなるわけで，w を求めるのはさらに 1 手順加わるに過ぎないのではないでしょうか？とくに 3.2.では p_1, q_1, 等，ほとんど w を求めるのに等しい議論をしているのでは思いますが．たとえば，(p_1, p_2 と同様に直ちに，求まる) r_1, r_2 を変曲点の位置として，w の代わりに，(r_1-r_2) を用いて議論するのではなぜいけないのでしょうか.

［著者］

ピークがすべて理想的な Gaussian や Lorentzian になっていれば，変曲点の位置を使って，w を求めることは可能です．しかし実際にはそのような誰の目で見ても分るピークをピークと判定できるのは当然のことで，実際にはピークかノイズかどちらにでも取れるようなギリギリの状態のピークを計算機で判定することに意義があり，また理論的な半値幅も一桁以上違っていることがしばしばあります．このような場合を考えますと，検出したピークのすべてについて半値幅 w を求め，それによってピークの検出条件を変えても結果的には大して変わりません．また実際には，スペクトルの平滑化や微分曲線を求める際に，途中で計算点数（w から求める）を変えることができません．もし無理に変えるとそこでこれらの曲線には段差がついてしまい，その段差のために全く存在しないピークをピークと判定してしまう危険性が大いにあります．このような事情から，常識的に考えると一見ピーク検出を行なう際に半値幅を求めて行う手法は良い様に思われますが，実際には殆ど効果を発揮できません．逆効果さえ出てしまいます.