Technical Report

Assessment of Peak Detection Algorithm Proposed by ISO/TC201/SC3 for X-ray Photoelectron Spectroscopy −Activity Report of VAMAS/TWA2/A9 Project "Evaluation of Procedures for Automated Peak Detection in X-ray Photoelectron Spectra"−

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(Received: March 8, 2007; Accepted: August 1, 2007)

The ISO/TC201 (Technical Committee of Surface Chemical Analysis)/SC3 (Data Management and Treatment) has proposed the algorithms of peak detection in XPS spectra. In order to evaluate these methods, we have developed a set of XPS spectra as an activity in VAMAS (The Versailles project on Advanced Materials and Standards)/TWA2 (Surface Chemical Analysis) committee. The artificial three kinds of XPS spectra were generated from the measured XPS spectra. Based on these spectra we have developed an additional set of 30 spectra that have the superposed statistically defined noises. Using this data set, we have also carried out the evaluation of the programs for the XPS peak detection, which provided by ISO TC201 SC3. In conclusion, we found many problems on the provided software that must be due to the use of un-appropriate parameters. In this software, it is impossible to select the other parameters because SC3 committee does not open its algorithm completely. Then, we concluded that the provided software is premature for practical use in XPS peak detection.

1. Introduction

Peak detection for XPS (x-ray photoelectron spectroscopy) spectra is required prior to the spectral analysis such as peak identification, chemical shifts, peak separation, peak intensities, and so on. It is inevitably required especially for unfamiliar spectra that are not treated in daily work.

In the standardization on the committee of ISO/TC201 (Surface Chemical Analysis) /SC3, the peak detection algorithms have been proposed and discussed. The ISO/TC201/SC3 had requested the VAMAS (The Versailles project on Advanced Materials and Standards)/TWA2 (Surface Chemical Analysis) committee to examine the effectiveness of the peak detection algorithms proposed by them as the standard procedures. The VAMAS/TWA2 established a project A9 entitled "Evaluation of Procedures for Automated Peak Detection in X-ray Photoelectron Spectra". In this project, test spectra were analyzed by the software which made of the algorithms proposed in the ISO activity. In the next step, the test spectra are analyzed by the data treatment software using a kind of peak detection that is utilized in daily analysis work, though it could be applied to the peak assignment and identification. This is the reason why the data analysis software does not explicitly include the peak detection function that is hidden behind the procedure of peak assignment/identification. We could estimate the efficiency of the usefulness of the peak detection algorithms whether a set of assigned/identified peaks is completely included in a set of detected peaks.

In the present report we propose a set of test spectra

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for peak detection procedure in XPS. We also show the results of analyses by the peak detection algorithms and software prepared in the ISO/TC201/SC3 activity.

2. Algorithms of peak detection

The ISO/TC201/SC3 has discussed the three methods for peak detection, which are briefly explained in Appendix of the present report. Peaks were detected by the software developed under the algorithms proposed in the ISO activity. The critical value k is a multiplicative factor of the standard deviation σ_b of the background intensity in a spectrum. Then, $k\sigma_b$ corresponds to the tolerance for automated peak detection. In other words, it denotes a noise level range in which the algorithms does not discriminate a peak and noise. Then k is a key parameter and plays an important role in this procedure. However, it has been fixed in the software because it was optimized in the previous study [1]. Details of k are described in Appendix. We should remark that the re-investigation of the optimization of k-value shall be done. We applied the three methods of “Spectrum Background Method”, “Peak Detection by Directly Calculating Peak and Background”, and “Peak Detection Using Threshold Curve of Second Derivative”, and they are abbreviated as “BGD method”, “PB method”, and “2nd DER method”, respectively. Principles of these three methods are explained in the Appendix chapter, though it is not known to us how to choose these three methods from various kinds of peak detection procedures in spectral treatment processing with a specified reason by the ISO committee.

3. Test spectra

We have made a set of test spectra from XPS spectra for Au, Ag, and Cu measured with monochromatic Al x-ray source. The energy step of the spectra is 0.5 eV for the binding energy region from 1200 eV to 0 eV. The spectrum “b001” was composed by a simple summation as I_{Au} (BE) + I_{Ag} (BE) + I_{Cu} (BE), where I (BE) denotes an intensity as a function of BE (binding energy). The spectra of “b002” and “b003” were also composed by the linear summation as $I_{Au}(BE) + 0.1 \times I_{Ag}(BE) + 0.01 \times I_{Cu}(BE)$ and $I_{Au}(BE) + 0.01 \times I_{Ag}(BE) + 0.001 \times I_{Cu}(BE)$, respectively. Figure 1 shows these three test spectra where the energy range is from 1200 eV to 0 eV and the unit of intensity axis is expressed in counts.

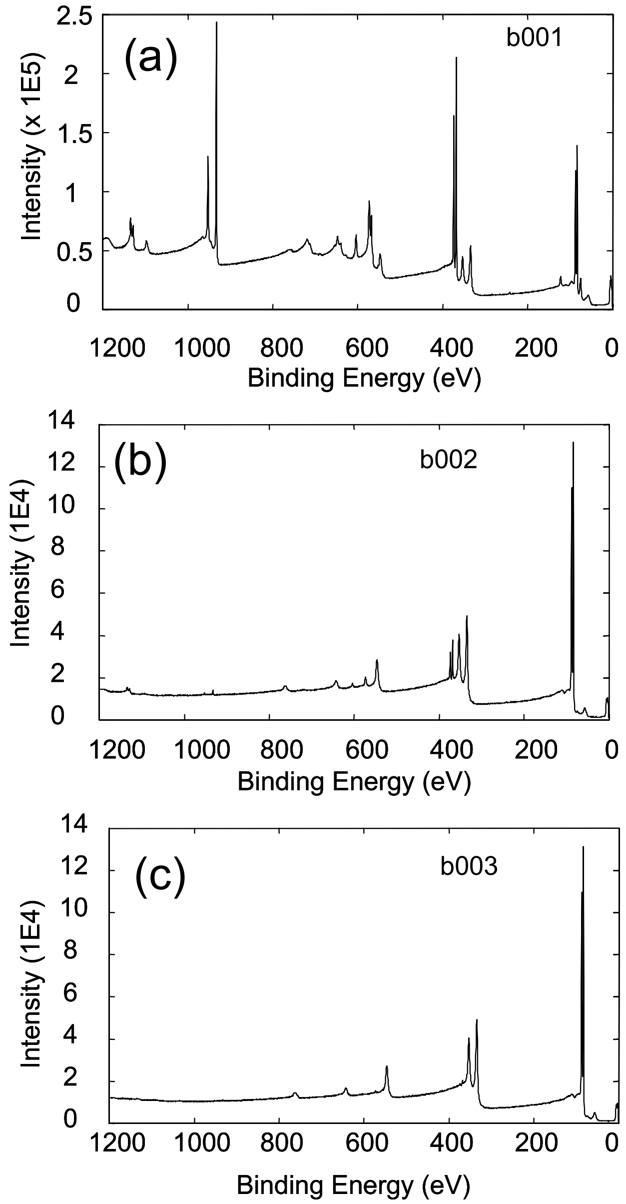


Fig. 1. Test spectra composed from the measured Au, Ag, and Cu spectra. The synthesis ration of the three elements (Au, Ag, Cu) is (1, 1, 1) for (a), (1, 0.1, 0.01) for (b), and (1, 0.01, 0.001) for (c).

As well known, the dispersion of the signal depends on the square root of its average value of the intensity at each channel in the case of any particle counting system. It is also consistent with total intensity given by the sum of the intensities over all channels of the spectrum because of the linear relationship. Thus, estimating the average intensity of the spectrum by means of some method, the dispersion of average should be also estimated with the same method.

The S/N of measured spectrum can be adjusted using above relationship. Then, it is necessary to separate sig-

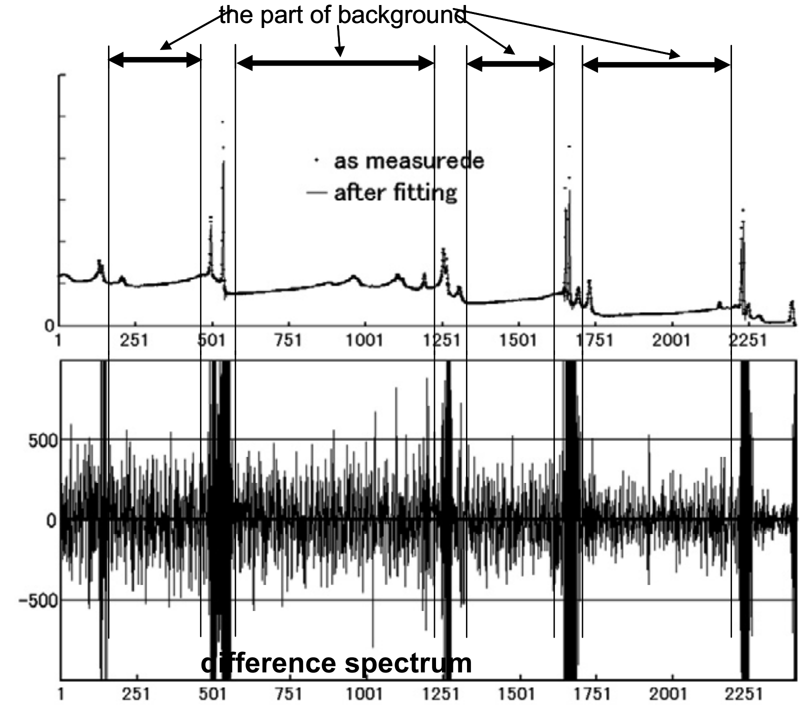


Fig. 2. Example of setting the region for appropriately calculating S/N.

nal and noise exactly, and this separation process is equivalent to the high-precision smoothing process. Then, we estimated the true signal without noise from the given spectra with the curve fitting method using cubic spline function. Therefore, the difference spectrum between the given (measured) spectrum and the fitted spectrum gives the noise of the given spectrum. The accuracy of the present method may deteriorate in sharp peak region. Thus, for the quantitative estimation of S/N for given spectrum, it is the most appropriate for obtaining the appropriate value for the definition to calculate from the given spectrum such as the background or the spectral region with no remarkable sharp and high-intensity peak, as shown in Fig. 2.

When the test spectra were considered as a normal distribution, the mean values are 0 and their standard deviations are given by the square root of the average intensity. Thus, adding a set of random number to the normal distribution, the value of the dispersion of the noise part of given spectrum could be adjusted. Adjusting the noise part to the true spectra, we can obtain the spectrum, which have the adjusted dispersion of the noise and average signal intensity, independently. This process becomes a basis of the method for adjustment of S/N for the measured spectrum.

The noise superposition procedure generated the ten spectra for each test spectrum, b001_7*n* and b001_4*n* (also, b002_7*n* and b002_3*n*, and b003_7*n* and b003_2*n*). *n* corresponds to the number of random number generation and from 1 to 5. The examples of noise superposed spectra, b003_21 from b003_2*n* (*n*: 1 to 5) and b003_71 from b003_7*n* (*n*: 1 to 5) are shown in Fig. 3.

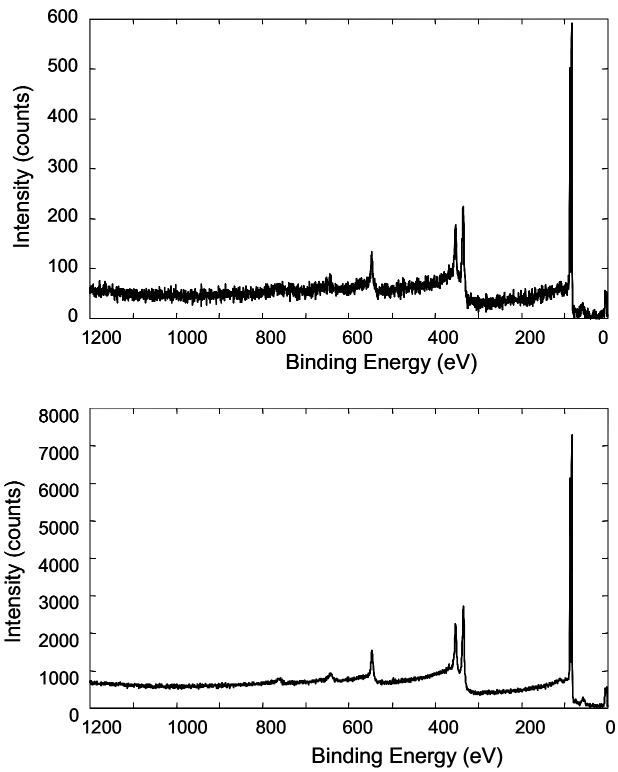


Fig. 3. Examples of artificial noise superposed spectra.

4. Results and discussion

The test spectra of b001, b002, and b003 were processed by the peak detection routines provided from the ISO/TC201/SC3 activity. The critical value k , the averaged distance in the BGD method, the parameters for derivative procedure in the PB method and the 2nd DER method were fixed in the analyses because the ISO/TC201/SC3 activity defines their recommended values.

Figure 4 shows an example of the results that was analyzed by the BGD method for b002. The vertical axis was expanded to recognize the small peaks detected in the figure. Using the ISO software, almost peaks were detected as multiple peaks at the same biding energy. When the spectrum b001 was analyzed by the 2nd DER method, the number of peaks detected at a binding energy was from 2 to 16. In the discussion session, plural peaks at a same binding energy were regarded as a single peak. Then the number of the detected peaks were reduces from 275 to 66 for b001 with the 2nd DER method.

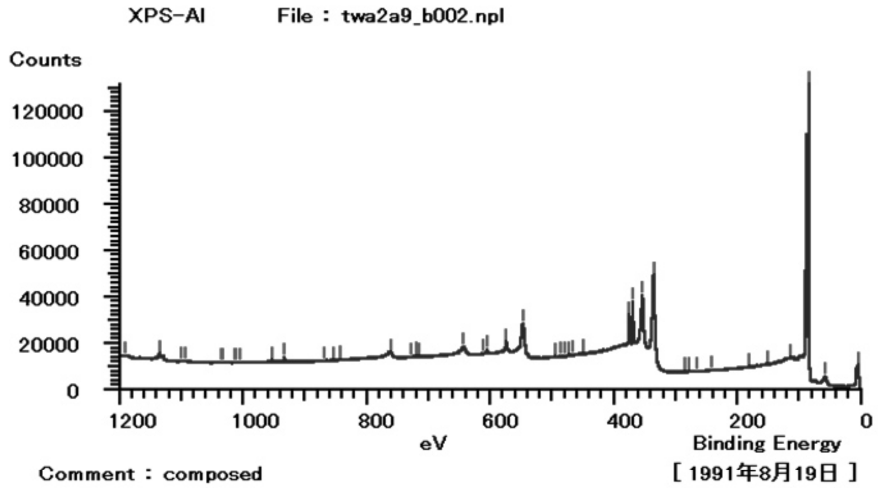
The peaks were detected by analyst's eyes as references for b001, b002, and b003 with his experience. In the manual procedure, a part of the spectra was expanded along the both directions along the horizontal and vertical axes. Figure 5 shows the peak positions detected by the analyst's eyes for the b001. They are categorized for the five ranks (SS: very strong, S: strong, M: medium, W: weak, WW: very weak). The resulting peak positions are also shown in Fig. 5 based on the three ISO algorisms. We see that many peaks are detected by the ISO software in the region where no peak is detected by the analyst's eyes especially for 2nd DER method. The number of the detected peaks by the PB method should be less than that predicted by the 2nd DER method in Fig. 5 because the PB method utilizes peak-background comparison procedure following the second derivative procedure (equivalent to the 2nd DER method).

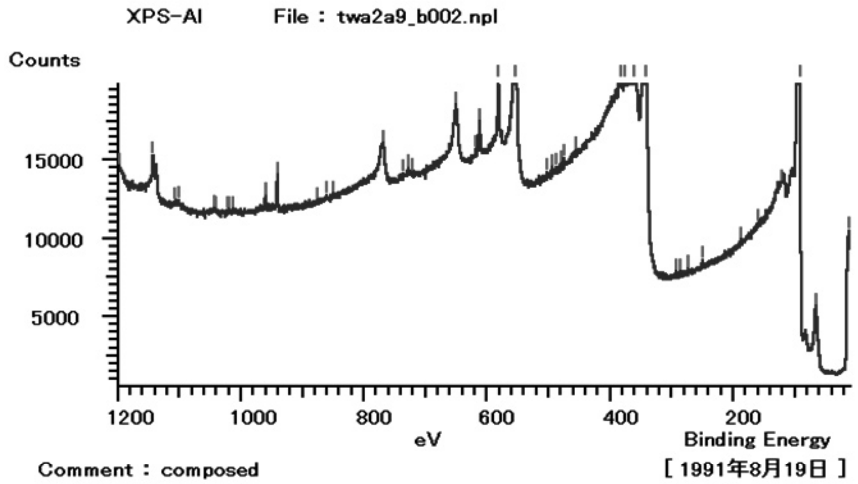
The numbers of detected peaks and the detectability* or the spectra of b001, b002, and b003 are plotted in Fig. 6 as a function of the normalized number determined from the eye-detection method. Taking the synthesis ratio of the three original spectra into the account, the number of detected peaks must be expected to be largest for b001 and smallest for b003. However, we obtain the contrary results when the BGD method are applied. The number of the eye-detected peaks is almost the same as that by the 2nd DER method for the spectra b002 and b003. On the other hand, the BGD or PB methods gave almost the same results. The quality of b001 seems to be different from that of b002 and b003. The numbers of the eye-detected peaks without the very weak ones are in good agreement with those by the PB method. The number of detected peaks and its detectability are plotted for the detection methods for the spectra b001 to b003 in Fig. 7. The detectabilities at the BGD method are almost unity for b001. On the other hand, those at the 2nd DER method are almost unity for b002 and b003. As noted above, the characteristics of b002 and b003 are similar with each other, but the result of b001 is different from them.

Figures 8 and 9 show the results of the peaks detected for the noise-superposed b001 spectrum. The amplitude of noise level is defined as mentioned in Section 3 and it is greater for b001σ4 than b001σ7. The numbers of peaks detected and their detectability are averaged for the five spectra generated by different randomness with the same amplitude.

The number of detected peaks drastically decreases below half (from 2 to 0.5) from the original b001 using the 2nd DER method. Even though we expected that the numbers of detected peaks and its detectability would be decreased when the noise amplitude was large, the detectability of b001σ4 using the BGD method is almost the same as the original one and greater than that of b001σ7. Here b001σ4 represents b001_4*n* (*n*: 1 to 5) and

*detectability: We define the term of "detectability" as the ratio of the number of detected peaks to that of eye-detected peaks instead of the true number of peaks in the spectrum of interest. The reason is that the true number of peaks in the spectrum is usually unknown. This is because a respective photoelectron peak generates loss peaks and a great number of Auger transition peaks are included in the spectrum [e. g. *Auger catalog*, by W. A. Coghlan and R. E. Clausing, *Atomic Data* **5**, 317 (1973)], though we can count the number of elastic photoelectron peaks in the specified binding energy range. On the other hand, even a noise looks like a peak if it has a suitable peak width and height. From these viewpoints, the term of "efficiency" might not be appropriate and one of the reviewers certainly suggested it as "detectability". Then we have changed the term of "efficiency" in the originally submitted manuscript to "detectability". The one of the reviewers additionally pointed out that a negative score should be given when a peak is detected at the position where it shall not exist. It will be taken into account in the next step of VAMAS/TWA2/A9.





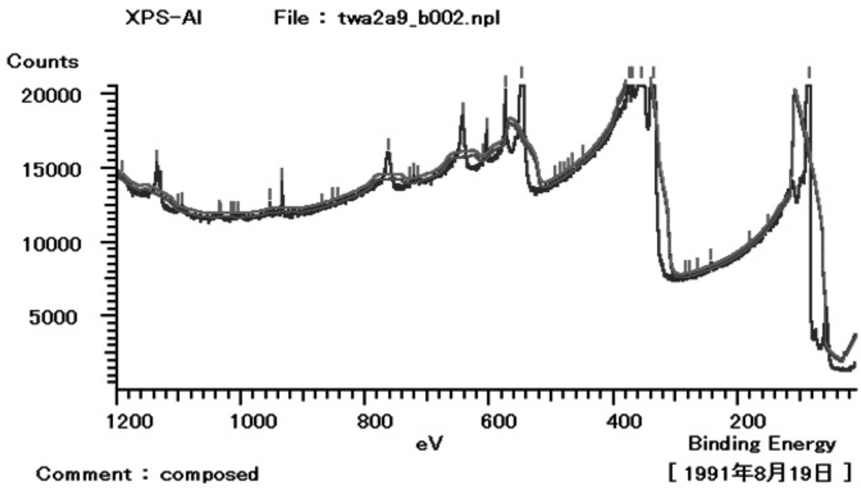


Fig. 4. The result of the peak detection algorism of the BGD method for the test spectrum of b002.

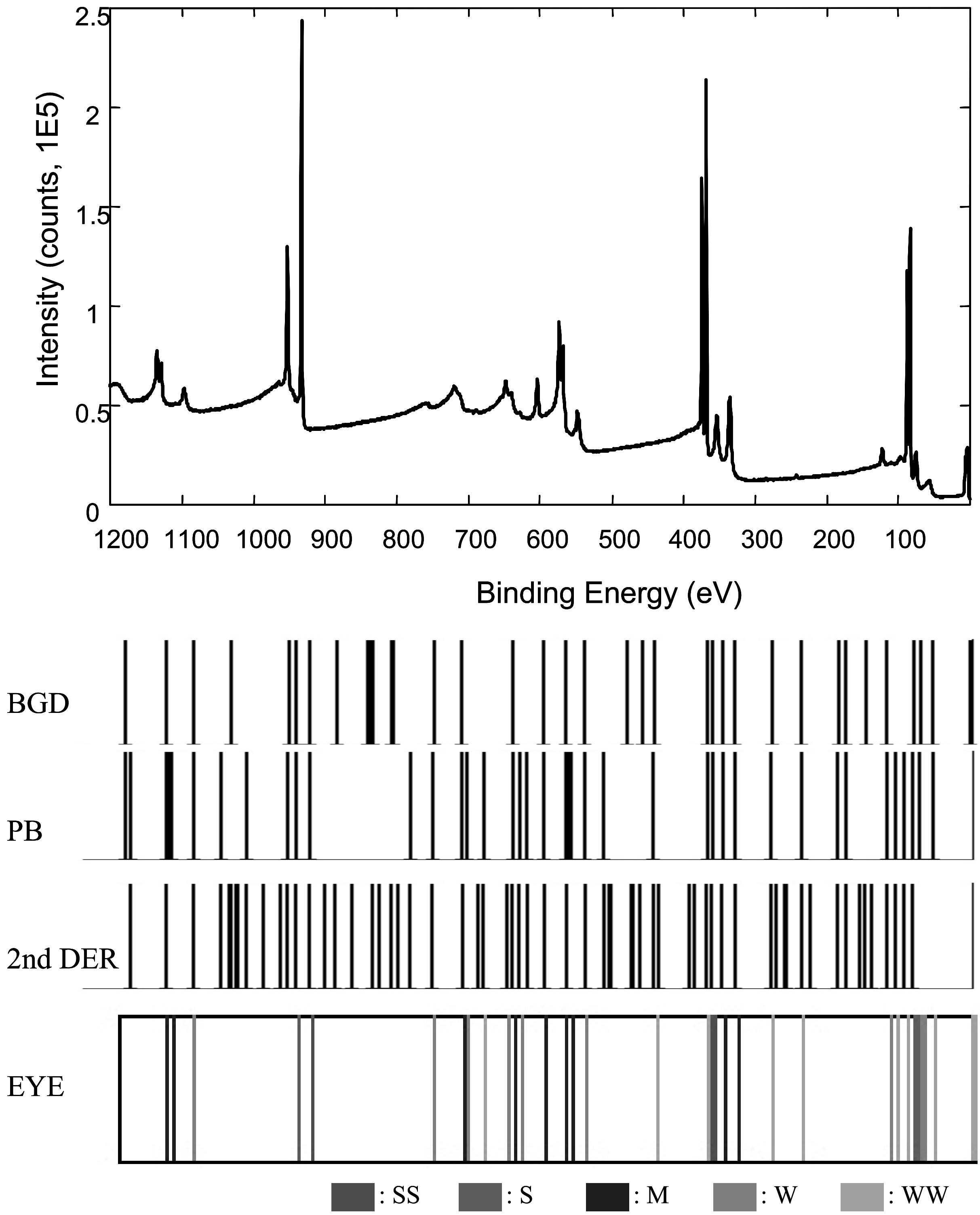


Fig. 5. The peak positions detected by the three methods for the test spectrum b001 and those detected by eyes.

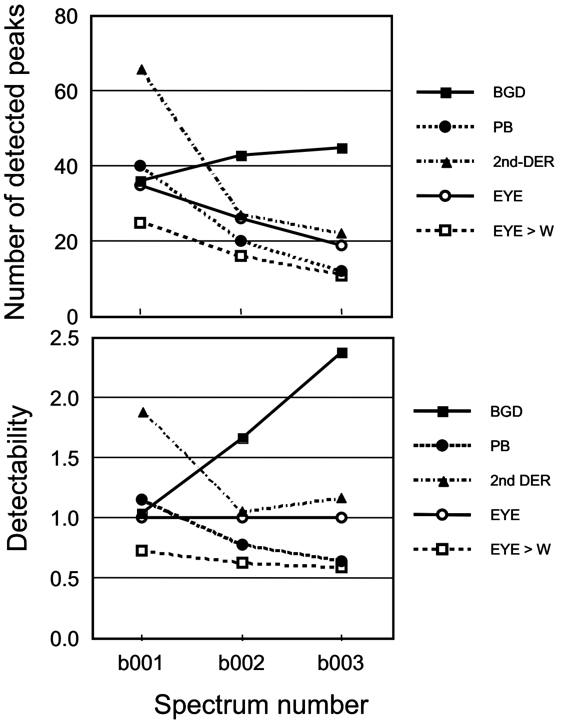


Fig. 6. The number of detected peaks for the spectra b001, b002, and b003. BGD, PB, and 2nd-DER correspond to the three methods proposed by the ISO activity. EYE means the total number of the detected peaks by the analyst's eye, and EYE>W denotes the number except the very weak (WW) peaks. Detectability is the normalized value by the number of detected peaks by the eye.

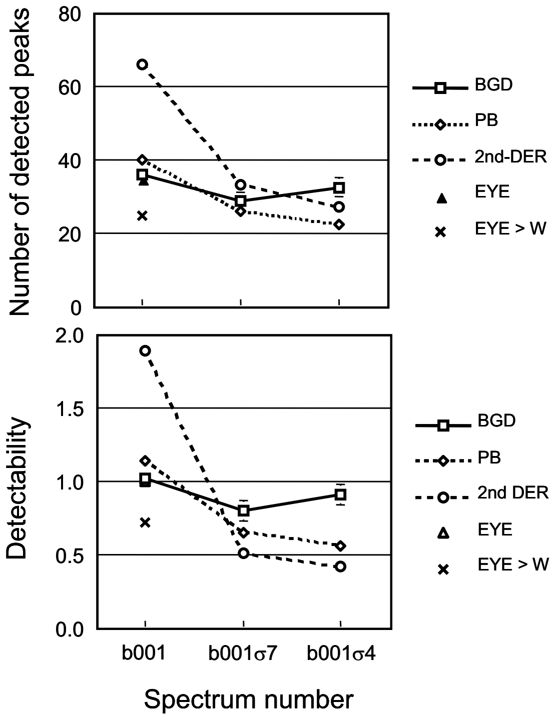


Fig. 8. The number of detected peaks for the spectra b001, b001σ7, and b001σ4. σ7 and σ4 means the artificial noise amplitude ($\sigma4 > \sigma7$) and they are averaged value for the five spectra generated by random number for b001σ7, and b001σ4. BGD, PB, and 2nd-DER correspond to the three methods proposed by the ISO activity. EYE means the total number of the detected peaks by the analyst's eye, and EYE>W denotes the number except the very weak (WW) peaks. Detectability is the normalized value by the number of detected peaks by the eye.

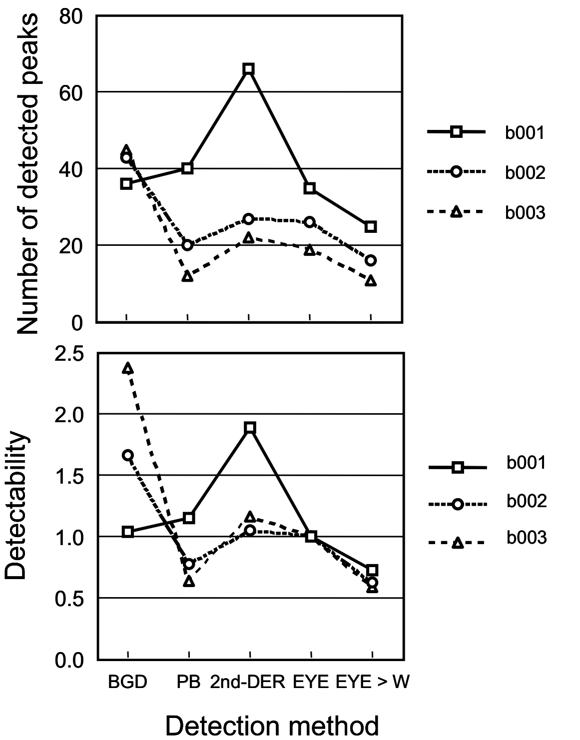


Fig. 7. The number and detectability are re-plotted against the detection methods for the spectra b001, b002, and b003.

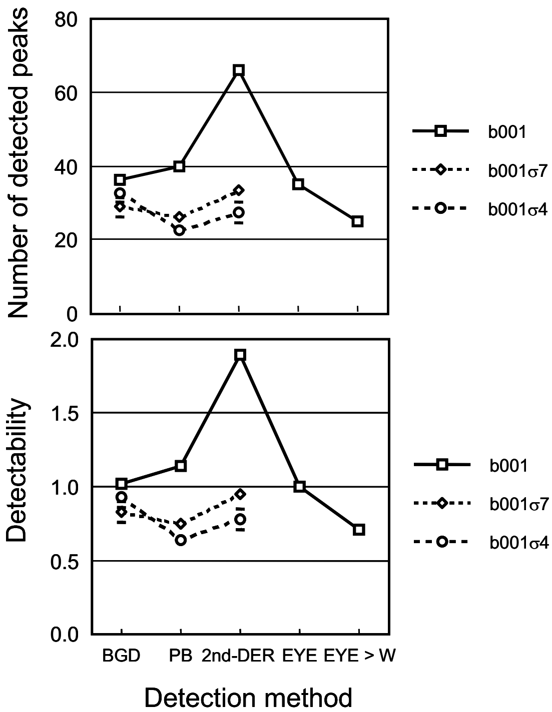


Fig. 9. The number and detectability are re-plotted against the detection methods for the spectra b001, b001σ7, and b001σ4.

b001σ7 does b001_7*n* (*n*: 1 to 5). The number of detected peaks for b00*m*σ*q* (*m*: 1 to 3, *q*: 2, 3, 4 or 7) means the averaged value of the numbers of peaks for b00*m*_*q*1 to b00*m*_*q*5 in this report,

$$b00m\_q = \left[\sum_{k=1}^{5} b00m\_qk\right] \Big/ 5$$

Using the PB and 2nd DER methods, the changes of those quantities are smaller than the BGD method for b001σ4 than b001σ7.

Figures 10 and 11 show the results of peaks detected for the noise-superposed b002. Figures 12 and 13 show the results for the noise-superposed b003 spectra. For these two spectra the numbers of detected peaks and their detectabilities are decreased when the noise amplitude increases. The changes of detected peaks and detectabilities with the BGD method when the noise is superposed are greatest in the three procedures for b002 and b003. But those are greatest using the 2nd DER method for

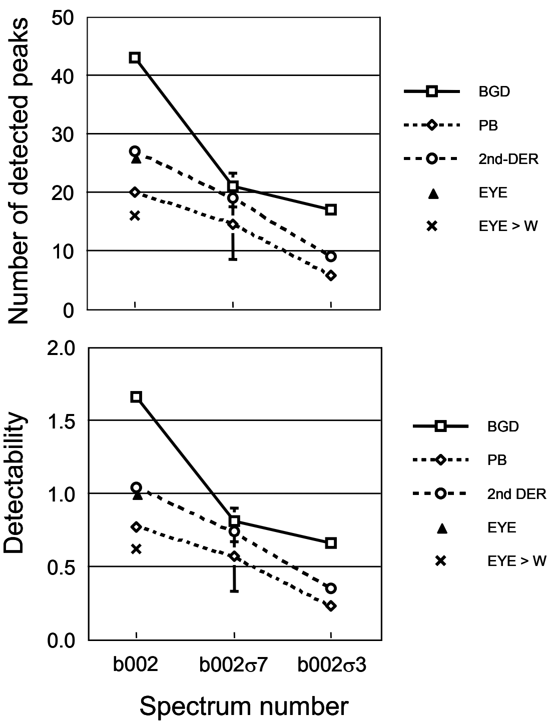


Fig. 10. The number of detected peaks for the spectra b002, b002σ7, and b002σ3. σ7 and σ3 means the artificial noise amplitude ($\sigma3 > \sigma7$) and they are averaged value for the five spectra generated by random number for b001σ7, and b001σ3. BGD, PB, and 2nd-DER correspond to the three methods proposed by the ISO activity. EYE means the total number of the detected peaks by the analyst's eye, and EYE>W denotes the number except the very weak (WW) peaks. Detectability is the normalized value by the number of detected peaks by the eye.

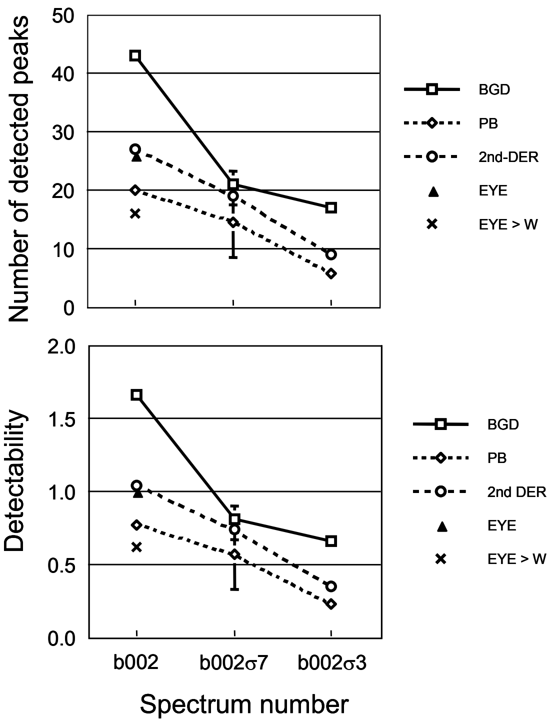


Fig. 11. The number and efficiency are re-plotted against the detection methods for the spectra b002, b002σ7, and b002σ3.

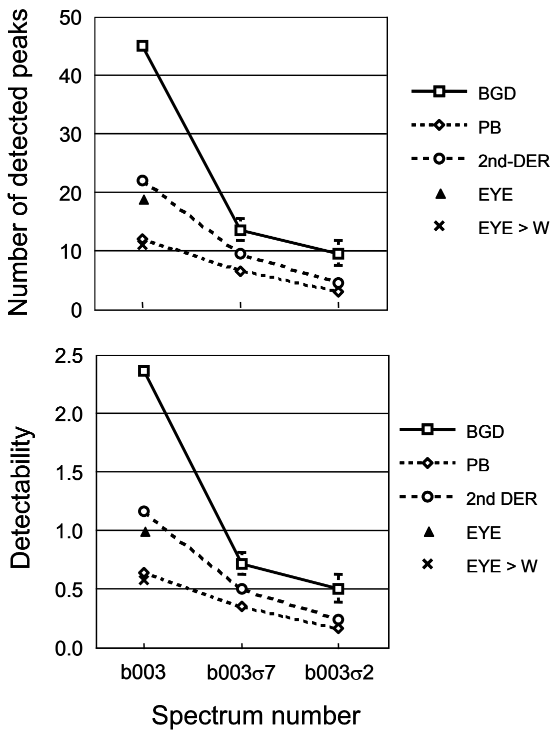


Fig. 12. The number of detected peaks for the spectra b003, b003σ7, and b003σ2. σ7 and σ2 means the artificial noise amplitude ($\sigma2 > \sigma7$) and they are averaged value for the five spectra generated by random number for b001σ7, and b001σ2. BGD, PB, and 2nd-DER correspond to the three methods proposed by the ISO activity. EYE means the total number of the detected peaks by the analyst's eye, and EYE>W denotes the number except the very weak (WW) peaks. Detectability is the normalized value by the number of detected peaks by the eye.

b001. The quality of the original b001 may be different from those of b002 and b003. It is hard to comprehend the origin of different characteristics, considering that they have been artificially composed from the same spectra. We can guess that the contribution of Ag components is so small for b002 than that for b001, even b002 includes about 10% contribution of Ag signals. The BGD method may be most sensitive for noise rather than the 2nd DER method and the PB method. The order of the detectability is BGD $\geq$ 2nd DER > PB for all of the test spectra, seeing Figs. 8 to 13.

5. Remarks for future work

Practically we do not use explicitly the peak detection routine with data analysis software that is distributed with XPS apparatus or stand-alone from the third party. We usually use a routine of peak identification or assignment where the peak detection process may be hidden behind it. In the next step in the VAMAS/TWA2/A9 activity it is planned to detect peaks or identify/assign peaks using daily used software by the RRT (round robin test) participants. When peak detection software is applied, the detected peaks will be compared with ones detected by the software proposed in the ISO activity. When peak identification/assignment software is applied, the identified/assigned peaks will be evaluated whether they are included within the peaks detected by the software proposed in the ISO activity.

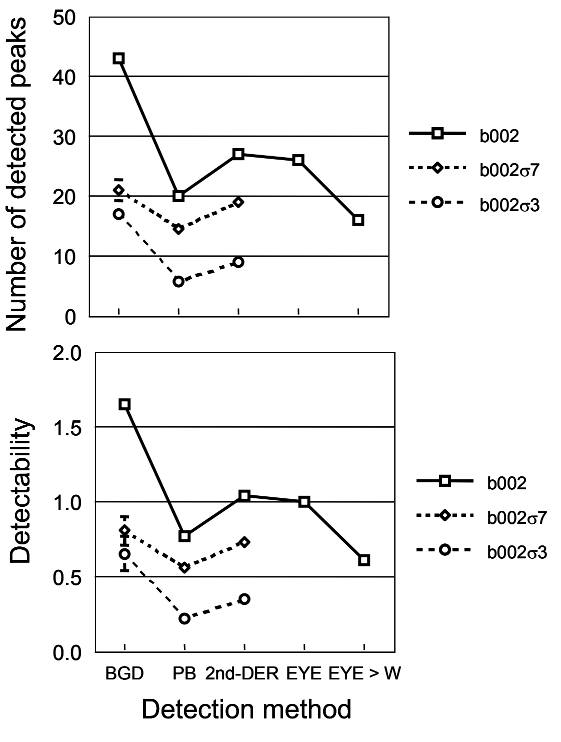


Fig. 13. The number and detectability are re-plotted against the detection methods for the spectra b003, b003σ7, and b003σ2.

6. Acknowledgements

The software in the ISO activity was mainly developed by Y. Nagatsuka (JEOL, Japan) and Y. Nagasawa (JEOL, Japan) and it was supported by Y. Furukawa (DENKA, Japan). The authors deeply express our gratitude to them and other participants in ISO/TC201/SC3 for the citation of peak detection procedures from the draft discussed. The authors also wish to thank C. J. Powell (National Institute of Standards and Technology, USA) for his continuous interest and encouragement. We also thank members of SASJ (The Surface Analysis Society of Japan) for their useful advice and helpful comments.

7. Statement from authors to editors

As we mentioned in the Introduction chapter, the ISO committee chose the three algorithms and made software in which variable parameters were optimized by them. Under ordinary circumstances the ISO committee should evaluate the efficiency of the algorithms, though it would be conducted by the new project in VAMAS/TWA2. The VAMAS committee made the set of test spectra and evaluated the efficiency. One of major conclusions is that the software provided by the ISO committee has not achieved a level at that efficiency can be examined and discussed.

The authors submitted the previous version of the present report to Journal of Surface Analysis and two reviewers critically read it and commented valuable issues. Most of essential substances in their comments except for editorial issues are inherent contents in algorithms and software. We could not revise our submitted manuscript because key contents in the reviewers' comments should be considered by the ISO committee and we had no choice but to withdraw it because the three authors were not directly related to discussions in ISO/TC201/SC3.

Now we submitted the present as an activity report done by the VAMAS/TWA2/A9 committee. This is because the VAMAS does not have an official reporting system like a journal and it is also appointed that it is important to publish a report as a record of the activity by several persons in the VAMAS committee. The present report has submitted after some revision according to reviewers' comments that can be judged by the authors in order to avoid scattering and losing investigated results.

8. References

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[5] Working draft ISO/TR22474 that is under discussion in ISO/TC201/SC3.

Appendix

The ISO/TC201/SC3 has proposed the three methods for peak detection and they are briefly explained in this chapter. The outline of the working draft of ISO/TR22474 [5] that is under discussion in ISO/TC201/SC3 is described below.

Algorithms of peak detection methods are broadly classified into 4 categories, namely, the moving average method, the multi-pass data scanning method, the derivative method and the curve fitting method. The moving average method and derivative method are adopted in the proposed methods. Using these two algorithms the three peak detection methods are proposed as a rough estimation of the background, direct calculation the peak and background relation at the candidate peak, and use of the second derivative curve.

A.1 Spectrum background method (BGD method)

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 (see Fig. A-1).

(1) Estimates the background intensity for each point of the spectrum. The background intensity is defined as the simple average intensity around each point of the spectrum. The number of averaging points is equal to several (5 to 10) times the number of points in the full width region at half maximum of the average peak of the spectrum.

(2) Calculates the standard deviation of the background intensity, σ_{bi}, and that of the measured spectrum, σ_{yi}.

(3) Estimates the difference (n_i) between the two by subtracting the background intensity from the spectrum intensity, where n_i is defined as: $n_i = y_i - b_i$. Here, b_i is the data point variance expressed by the previous work [2].

(4) Calculates the standard deviation (σ_{ni}) for the net (subtracted) intensity.

(5) The final inequality for judging the existence of a peak is defined as follows:

$$n_i > k\sigma_{ni}$$

where critical value k is normally equal to a value from 2 to 3 and is arbitrarily set depending on the spectrum conditions. The maximum peak is detected in the region where the inequality $n_i > k\sigma_{ni}$ holds.

(6) For small and broad peaks, further data processing is effective.

Calculates area S_{i0} for a typical noise peak by multiplying the full width at half maximum of the average peak by the noise intensity. Calculates peak area S_i in the region where $y_i - b_i$ is positive but does not exceed $k\sigma_{ni}$. If the inequality $S_i > S_{i0}$ holds, the peak is determined to be real.

(7) 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.

A.2 Peak detection by directly calculating peak and background (PB method)

In this method, the candidate peaks are detected by the second derivative treatment and judged by comparison with criteria. (see Fig. A-2).

(1) Calculates the second derivative curve for the spectrum.

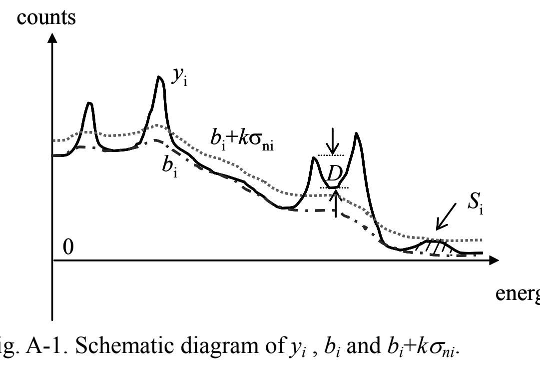

Fig. A-1. Schematic diagram of y_i , b_i and $b_i+k\sigma_{ni}$.

(2) Calculates the standard deviation (σ_i,) for the second derivative curve using the Savizky-Golay method [3].

(3) A candidate peak is deemed to be detected if the local minimum of the second derivative exceeds (in absolute value) one third of the threshold noise level ($k\sigma_i$, /3).

(4) The first and fourth zero-cross positions among four zero-cross positions in the second derivative curve around the candidate are regarded as both sides of the background positions of the candidate peak.

(5) Uses the background intensities at both sides of the background positions for estimating the background intensity of the candidate peak.

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

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

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 calculated as

$\sigma_N^2 = P + (B_1 l_2^2 + B_2 l_1^2)/(l_1+l_2)^2$ [4].

(7) If the difference between the candidate peak and the background intensity at the peak position is lager than k times its standard deviation, a peak is detected.

$$N > k\sigma_N$$

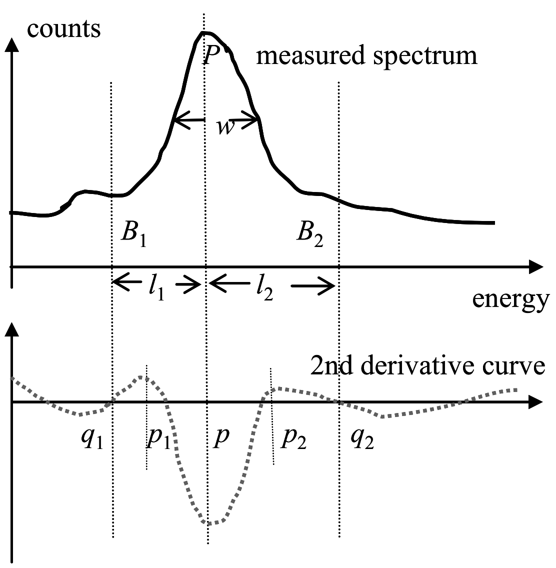

Fig. A-2. Schematic diagram of a peak position and both sides of the background.

(8) 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 admit the position with a distance of 3 times the peak width from the candidate peak position as a background position for the peak.

A.3 Peak detection using threshold curve of second derivative (2nd DER method)

This method has the same effect as subtracting the background from the spectrum by making use of the second derivative. As the algorithm has no arbitrariness in the background subtracting procedure, it may be relatively convenient when it is used with a computer (see Fig. A-3).

(1) Calculates the second derivative curve, d_i., for the spectrum, y_i.

(2) Calculates the standard deviation of the second derivative curve, σ_i.

(3) As the peak in the spectrum corresponds to the local minimum of the spectrum, the peak is deemed to be real if the local minus minimum $d_{\min}$ is less than (or greater than in absolute values) the noise fluctuation. For peak determination, therefore, the peak is deemed to be detected at the position that gives $d_{\min}$ in the second derivative if the following inequality is satisfied.

$$d_{\min} < k\sigma_i$$

Proposed peak detection methods for a spectrum are not fully perfect method but have practical uses as shown below. The relative merits of each method are shown in Table A-1.

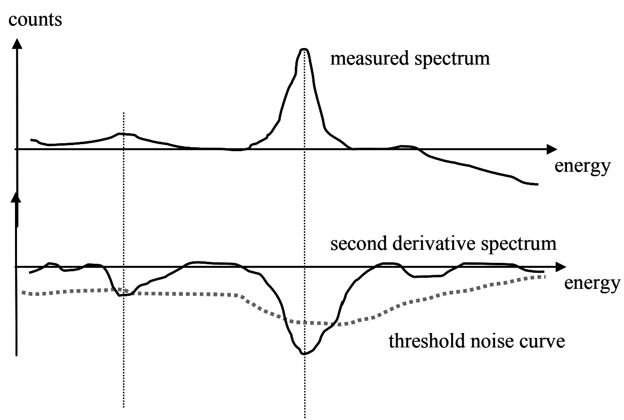

Fig. A-3. Schematic diagram of a peak position, second derivative curve and threshold noise curve.

Table A-1 Relative merits of each method.

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

査読コメント

査読者 1. 吉原一紘（アルバック・ファイ）

本論文は，通常の原著論文とはことなり，VAMAS/TWA2/A9 の技術レポートであり，ピーク検出に関する試験結果の報告を主としています．本レポートに記述されている結果は,ISO の規格作成の際に参照する必要がある有用なデータですので，JSA に掲載すべきであると思います．ただし，ピーク検出法のアルゴリズムの説明については不十分であることを指摘せざるを得ないので，アルゴリズムに関する解説記事を別に掲載することを勧めたいと思います．なお，編集上の問題がいくつかありましたので，以下に検討すべき箇所を指摘しておきます．

［著者］

実際に本報告を記述していて，困ったのはアルゴリズムを説明できる引用文献がないことです．要点のみ記述したつもりですが，読者には理解しづらいことにかわりはないと思っています．本文中にも記述しましたが，アルゴリズムは ISO/TC201/SC3 に対応する国内委員会で検討が進められてきていますので，解説記事は関係者に報告してもらうのが良いと考えます．査読者のコメントを勘案して，JSA 編集委員会から，ISO/TC201/SC3 対応国内委員会に原稿を依頼していただけないでしょうか．

［編集部］

アルゴリズムに関する記事を次号へ掲載します．

［査読者 **1-1**］

104 ページ「2. Algorithms of peak detection」の 5 行目の「critical value *k*」の意味を Appendix を参照しなくても理解できるように，簡単な説明を本文中にも記述していただけませんか.

［著者］

ごく簡単に説明文を加えました（104 ページ「2. Algorithms of peak detection」の 5－14 行目）.

［査読者 **1-2**］

Fig.2 の caption が不十分であるため, 105 ページ右カラム下から 3 行目から右カラム上から五行目に至る文章を理解することが困難です．caption を充実させるか，あるいはこの箇所の記述を充実させてください.

［著者］

別紙参照下さい.

［査読者 **1-3**］

検出したピーク数を「目」で検出したピーク数で規格化した値を efficiency としています．efficiency が 2 から 0.5 となって向上したと記述されていますが，数が減少することが上昇するという表現は，「efficiency」の持つ語感とは違和感があります．「efficiency」をより適切な言葉で置き換えてはどうでしょうか.

［著者］
後藤先生から「detectability」という用語の提案がありましたので，著者で相談の上，用語を変更しました．ただし，「有効性評価」という意味合いの部分は efficiency のままにしました．また，efficiency の向上の部分に関しては，footnote として注記を加えました．また，図中の用語も efficiency から detectability に変更しました．

査読者 2．後藤敬典（AIST 中部）
実用上も学問的にも大変興味のある大題でぜひ確立していただきたいものです．

［査読者 **2-1**］
efficiency (detectability?), community (comittee?) はいいでしょうか？
［著者］
detectability, committee への用語変更は参考にさせていただき，修正しました．

［査読者 **2-2**］
内容でコメントしたいのは，Noise の性質です．これをキチンとしておけば ISO 的に普遍的なドキュメントになると思います．講演会でも質問したのですが，お答えは，ガウス的な雑音でキチンとしているということでした．これは確率の性質ですので，平均値，標準偏差（実効値）で数値として与えるべきで，これがあれば比較が意味を持ってきます．完全なガウスでは議論ができませんので，周波数範囲（に相当するもの；エネルギースッテップの逆数）も与えるべきでしょう．
［著者］
別紙を参照下さい．

［査読者 **2-2-2**］
判定の基準として‘Efficiency’で評価していますが，述語ならこだわりませんが．あるべきスペクトルを‘ある’と判定するのはわかるのですが，ないものを‘ある’と判定したときは‘0’よりもペナルティを加えるような判定のほうが現実味があると思うのですがいかがでしょうか．
［著者］
興味あるコメントだと思います. ただ現段階では，どれが「ないもの」を「ある」と判断したのか，判定ができません．ですので，コメントを本文中の脚注に含め，今後のラウンドロビン活動のまとめの中で negative score を与えることを検討したいと思います．

［著者からの別紙回答］
ご指摘に対してお答えするには，実際に使用したデータの一部をご紹介する方が早いかと思われます．本文中にもありますが，ノイズを与えるための手がかり（数値的基準）として，それぞれの実測スペクトル中の特定のピークを指定し，そのピークがノイズに隠れるかどうかでシミュレーションスペクトルを作製しています．
例えば，Au:Ag:Cu=1:1:1 で合成したスペクトルでは，スペクトル中に現れる Ar 2p のピーク強度を，ノイズ調整のスケールとして利用しています．図 Q&A-1 に示すのは，Au:Ag:Cu=1:1:1 で合成したスペクトル中の Ar 2p の部分を拡大したものです. Spline による平滑化処理を行った後で，ピーク両側の立ち上がりの共通接線となるようなバックグラウンドを決め，元のデータにおけるピークの最大値を与える位置 x でのバックグラウンド強度 I と，信号強度 A に相当する値を決めます. 例えば, スケーリングファクターを k としたとき，位置 x での強度を新たに $k\cdot I$ と置いたとき，この強度を持つ信号の伴うばらつきの標準偏差σは$\sqrt{k\cdot I}$ で見積もられます．このσが A の何倍になるかで，逆に k を与えることが出来ます．
図 Q&A-2 には，A が 1σ相当から 7σ相当までに対応した k で決められる条件でスペクトルに最終的に与えられたノイズについて，それぞれの度数分布とその分布から求めた標準偏差を示します．データ点数が同じですので分布の面積が一定となるため，S/N の良い条件になるほど分布が平坦となり，元のデータのノイズ分布に近づいていくことがわかりま

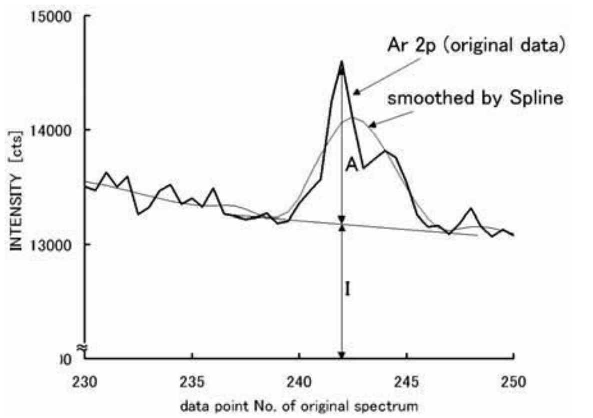

Fig. Q&A-1.

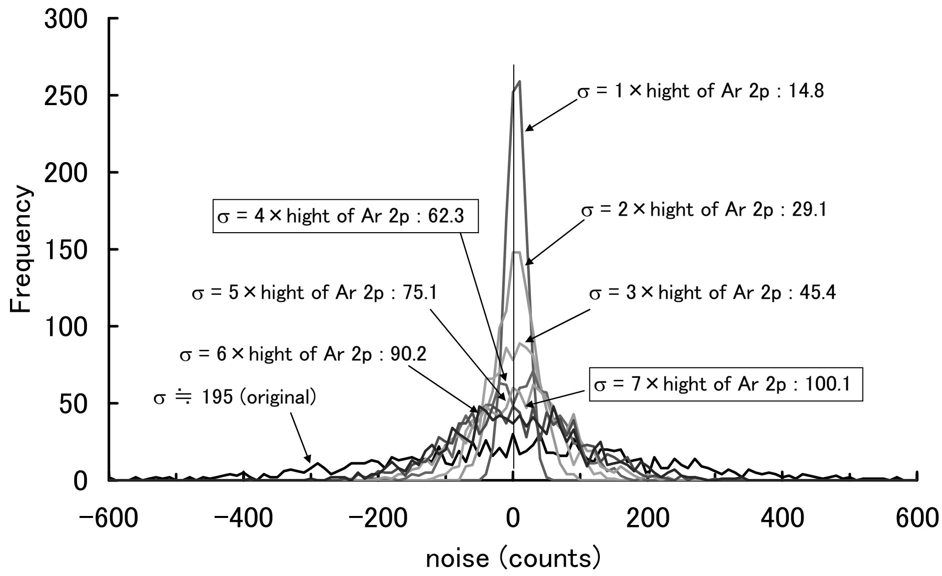

Fig. Q&A-2.

す. また, いずれの場合も平均値はほとんど 0 を取っており, 元のノイズ成分（図中の original と示されたもの）の分散だけを調整していることがわかると思います. 本文でのシミュレーションデータとしては, このうちの A=4σ（ほぼ Ar 2p がノイズに埋もれている）と A=7σ（もとのデータより若干 S/N が悪い）を仮定した条件を採用しているわけです.

図 Q&A-3 には, 元のデータと採用した 2 つのデータのノイズ成分の周波数空間での振る舞いを示しています. ノイズの定義として, 信号強度の変動も周波数空間での変動もランダムであること（一種のエルゴード性）が重要です. 図 Q&A-3 を見ますと, 元のデータは低周波領域で若干落ちている（ここに本来のスペクトルの成分が存在する）もののほぼ周波数空間全域でランダムに変動していることがわかります. また, シミュレーションデータとして使用したデータ用に調整した 2 系統のノイズデータも, 全周波数帯域でランダムに変動しており, ノイズ本来の性質を保持していることがわかります. 他のシミュレーションデータに関しても, まったく同じ知見を得ることができます.

以上の説明でおわかりの通り, ノイズに関しましては, 平均値はほぼ 0 で与えられなければなりませんから（図 Q&A-2 で示しましたとおり, それは満足されていますので）, 分散（もしくは標準偏差）が数値として与えられるべきデータということになります. ここでは, それにかわる値として A=$n\sigma$としたときの n の値を用いたわけです.

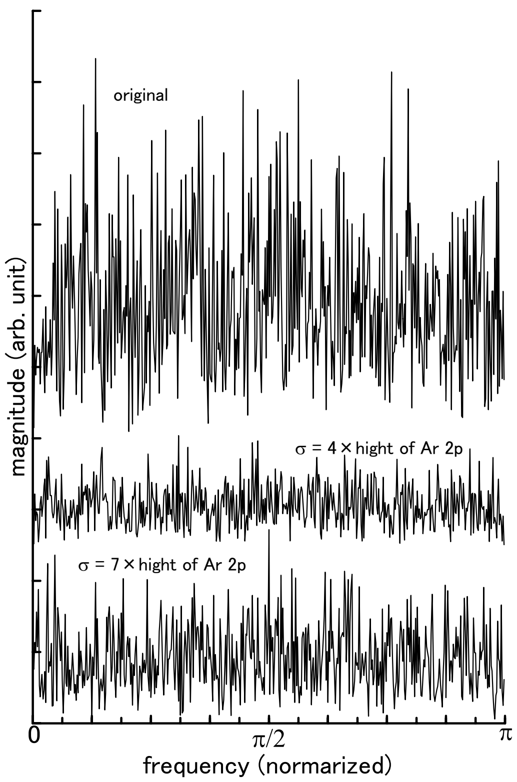

Fig. Q&A-3.