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On Detection Limit by Parallel Electron Energy Loss Spectrometer

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We developed the interface and software to control the parellel electon energy loss spectrometer recently developed by Gatan. Performance of the parallel detector was analyzed based on the statistical model. Although this system is not adequate to count each electron, it was estimated that for light elements the minimum detectable mass (MDM) is smaller than that estimated by Isaacson and Johnson [Ultramicros. 1, 33 (1975)]. The detectable minimum mass fraction (MMF) is proportional to the peak to background (P/B) ratio. On the parallel detector, the P/B ratio is determined by the channel-to-channel gain variation v_g. The gain variation of our detector is measured to be about 2%, and thus the attainable P/B ratio from a single raw spectrum is limited to about 5%. However, for a suitable specimen the MMF of about 10^{-4} (100 ppm) can be obtained by applying the least square fitting to the data which is a sum of the multiple read-outs on different channels after the correction of the channel-to-channel gain variation.

KEY WORDS: Parallel EELS/ Detection limit/ DQE

1. INTRODUCTION

A common analyzer commercially made for electron energy loss spectroscopy (EELS) uses the magnetic sector[1] to disperse electrons according to their energy. Here, an electron energy loss spectrum is usually measured sequentially by changing the current of the magnet. Recently, a new electron energy loss spectrometer (Gatan 666)[2], which measures a part of the spectrum simultaneously, has been made available. It has been shown that this spectrometer matches the serial spectrometer in the detective quantum efficiency (DQE), the dynamic range and the energy resolution[2]. Thus, the parallel detection of the spectrum will expand the application of EELS.

We have developed the interface and software to control the spectrometer by a micro-computer. One of the applications of this system will be reported elsewhere[3].

In this report, we first describe the interface and software developed to control Gatan 666. Next, we statistically analyze the performance of the parellel detector, and estimate its detection efficiency. Finally, we discuss the detection limits, MDM and MMF, imposed by this parallel electron energy loss spectrometer (PEELS).

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2. DEVELOPMENT OF MICROCOMPUTER INTERFACE AND SOFTWARE

The Gatan 666 spectrometer communicates with a multi-channel analyzer (MCA), which might be a microcomputer, through the 16-bits parallel I/O with the capability of direct memory access (DMA). To make the PEELS design concrete, Gatan has selected the interface using Q-bus to communicate with the microcomputer[4]. Although the microcomputer (Anritsu Packet IIe), which we have used to control the serial spectrometer[5], has a different external bus using a different communication procedure (the protocol), its parallel I/O interface can cope with the specifications required to the interface[4]. Therefore, we developed a protocol convertor (see Fig. 1), which was also designed as a bus convertor.

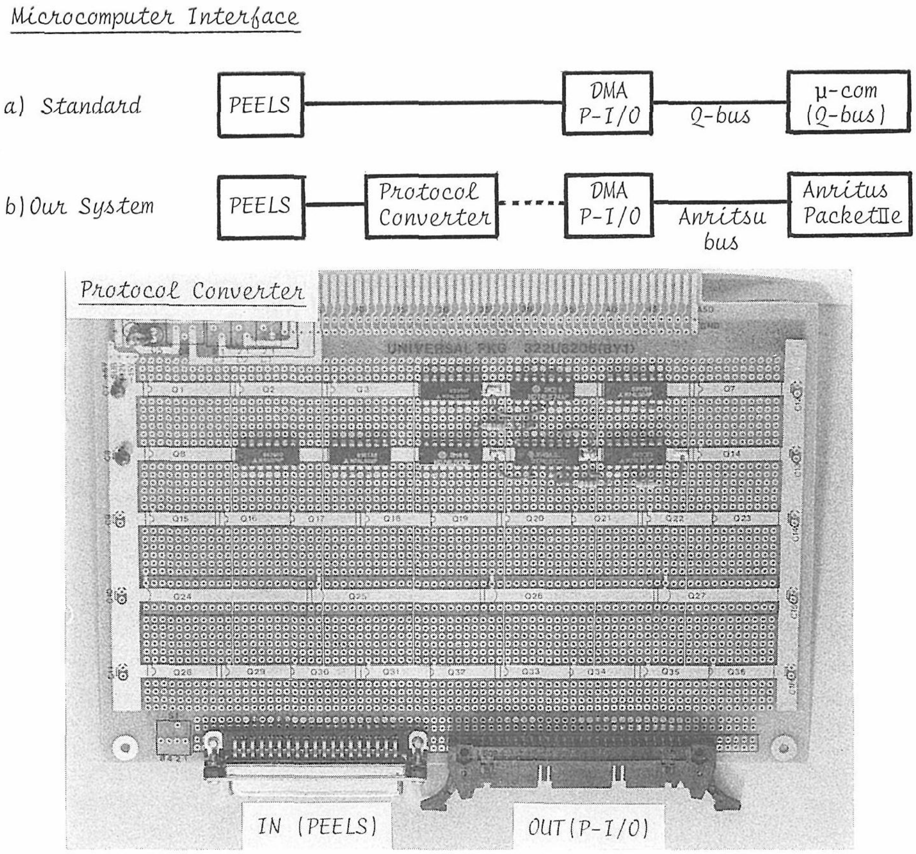

Fig. 1. An MCA (microcomputer) interface of our system.

A suit of software to align the spectrometer and to collect spectra was developed mainly based on BASIC. However, some routines, which require a high performance, were written with an assembler language and are linked with the BASIC programs. A special requirement for the MCA software is to display the spectrum rapidly (at least, several spectra per second) during the spectrometer alignment. Most recent microsomputer like ours can cope with such requirement, but normally requires the high standard of programming.

3. STATISTICAL ANALYSYS OF PARALLEL DETECTOR

The parallel detector of Gatan 666[2] consists of a single-crystal YAG scintilator and a linear photodiode array (PDA) (see Fig. 2). The spectrum is projected on the YAG sintilator, and the emitted photons are transfered through optical fibers to the photodiode array, which has 512 or 1024 channels. Table 1 shows some essential features of the PDA[2] of 1024 channels.

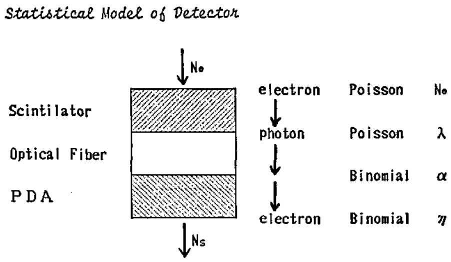

Fig. 2. The Structure of the parallel detector and its statistical model.

Table 1. Some performance parameters of PDA of 1024 channels. All the values are shown as photodiode electrons

Saturation Charge	5×10^7 electrons
Dark current	6×10^4 electrons/sec (10fA) at $-30°C$
Read-out Noise	3,500 electrons

3.1 Statictical analysis

If the parallel detector is ideal, its detection efficiency compared with the serial detector is improved by a factor equal to the number of channels. However, each channel of the parallel detector may have different performance, which will affect the detection efficiency. At first, we statistically analyze each channel of the parallel detector.

Here, we assume the following statistical model for the signal N_s: Poisson distributions for both the number of incident electrons (N_e) and the photon yield (λ) of the sintilator; and binomial distributions for both the transfer efficiency (α) of the optical-coupling and the photon-electron conversion efficiency (η) of the photodiode array. Furthermore, we assume a Poisson distribution (N_d) and a normal distribution N_r (m_r, σ_r) for the dark current and the read-out noise, respectively. The former results from the thermal electrons inside the PDA, and is a function of the temperature. Its output is proportional to the integration time. On the other hand, the latter has two sources of noise: the quantization of the signal into a 14-bits number and the electronic read-out circuit.

Thus, the raw output data N_t is the total of the signal, the dark-current and the read-out noise: $N_t=N_s+N_d+N_r$. Then, the average and variance of the output N_t of each channel are given by

$$\langle N_t\rangle=gN_e+N_d+m_r, \text{ and}$$

$$\sigma_t^2=\langle N_t^2\rangle-\langle N_t\rangle^2=(g^2N_e+gN_e)+N_d+\sigma_r^2\simeq g^2N_e+N_d+\sigma_r^2,$$

recpectively, where g is the gain factor defined as $g=\eta\alpha\lambda$. The two terms within the brackets show the variance of the signal, $\langle N_s^2\rangle-\langle N_s\rangle^2$, which is calculated straightforwardly by estimating the squared average of the assumed statistic process[6] successively. The gain factor of our detector system is around 200 for 100 keV electrons, since $\lambda\simeq 2{,}000$, $\alpha\simeq 15\%$ and $\eta\simeq 70\%$[2]. Thus, we get the last approximate equation.

In order to get the signal output S, we have to measure the output $(N_d'+N_r')$ without any incident electrons $(N_s'=0)$, and subtract it from the total output: $S=N_t-(N_d'+N_r')$. Then, the average and variance of the signal output are given by

$$\langle S\rangle=gN_e=\langle N_s\rangle, \text{ and}$$

$$\sigma_s^2=\langle S^2\rangle-\langle S\rangle^2=(g^2N_e+gN_e)+2N_d+2\sigma_r^2\simeq g^2N_e+2N_d+2\sigma_r^2,$$

Thus, the DQE is given as follows

$$\mathrm{DQE}_s=(S/N)_{\mathrm{out}}^2/(S/N)_{\mathrm{in}}^2\simeq g^2N_e/\{g^2N_e+2(N_d+\sigma_r^2)\},$$

since $(S/N)_{\mathrm{out}}=\langle S\rangle/\sigma_s$, and $(S/N)_{\mathrm{in}}=N_e/N_e^{1/2}=N_e^{1/2}$. When the input electrons satisfy that $N_e>2(N_d+\sigma_r^2)/g^2$, the DQE is almost ideal (>0.5). However, when the gain factor and/or the dark current vary from channel to channel, these variations behave as the noise if they can not be eliminated. Next, we analyse these channel-to-channel variations statistically.

We assume the normal distributions for the channel-to-channel variations of both the gain $g(m_g, \sigma_g)$ and the dark current $N_d(m_d, \sigma_d)$. Note that the channal-to-channel variation of the read-out noise, if any, can be included in the above two channel-to-channel dependences. Thus, the average and variance of the signal of the multi-channel are given by

$$\langle\!\langle S\rangle\!\rangle_m=\langle gN_e\rangle_m=m_gN_e$$

$$\begin{aligned}\sigma_m^2&=\langle\!\langle S^2\rangle\!\rangle_m-\langle\!\langle S\rangle\!\rangle_m^2=\langle\!\langle N_s^2\rangle+2N_d+2\sigma_r^2\rangle_m-\langle N_s\rangle_m^2\\&=\{(m_g^2+\sigma_g^2)(N_e^2+N_e)+m_gN_e-m_g^2N_e^2\}+2m_d+2\sigma_r^2\\&=\sigma_g^2(N_e^2+N_e)+N_e(m_g^2+m_g)+2m_d+2\sigma_r^2\end{aligned}$$

respectively. Here, the inside brackets $\langle\ \rangle$ shows the average at one channel, and the outside brackets $\langle\ \rangle_m$ the average over all the channels. The terms which include σ_g are the artificial noise due to the channel-to-channel gain variation. One of these terms is proportinal to N_e^2, and thus becomes a cardinal noise for a strong signal. While the artificial noise due to the channel-to-channel dark-current variation does not appear on the signal variance σ_m^2. This is because the signal S is obtained by subtracting the dark-current from the raw output data N_t. However, this output N_t for a prolonged intergration time will be heavily affected by the artificial noise σ_d^2, because the variance of the channel-to-channel variation of the dark-current itself is given by

$$\sigma_m(N_d)^2=\langle N_d^2+N_d\rangle_m-\langle N_d\rangle_m^2=\sigma_d^2+N_d.$$

To compare the average and variance of the multi-channel signal with those of the single-channel signal, we replace m_g and m_d by g and N_d, respectively. Then, the average signal $\langle\langle S\rangle\rangle_m$ over all the channel has the same expression derived for the single channel. When we further replaced σ_g^2 by $v_g^2g^2$, the variance becomes

$$\sigma_m^2 = v_g^2g^2(N_e^2+N_e)+N_e(g^2+g)+2N_d+2\sigma_r^2,$$
$$\simeq v_g^2g^2N_e^2+N_eg^2+2(N_d+\sigma_r^2).$$

Here, v_g^2 is the relative variance of the gain variation. Because v_g is typically 1-5% and $g\simeq 200$ for this system, we get the last approximate expression.

With this approximate expression of the variance, the DQE of the multi-channel detector is written as

$$\mathrm{DQE}_m \simeq g^2N_e/\{v_g^2g^2N_e^2+N_eg^2+2(N_d+\sigma_r^2)\}.$$

Thus, for low signals, i.e. $v_g^2N_e \ll 1$, DQE_m reduce to DQE_s.

It should be noted that the maximum number of the incident electrons (100 keV) for each channel is limited to about 3×10^5 owing to the saturation of the PDA. In order to measure more electrons, we have to use the multiple read-out. The multiple read-out is however straightfoward by using the PDA interface of this spectrometer. The average and variance of the sum of n signals from each read-out are given by

$$\langle\langle S(n)\rangle\rangle_m = ngN_e$$
$$\sigma(n)_m^2 = \langle\langle S(n)^2\rangle\rangle_m - \langle\langle S(n)\rangle\rangle_m^2$$
$$= v_g^2g\{(nN_e)^2+nN_e\}+nN_e(g^2+g)+2nN_d+2n\sigma_r^2,$$
$$\simeq v_g^2g^2(nN_e)^2+nN_eg^2+2n(N_d+\sigma_r^2)$$

Then, since $(S/N)_{\mathrm{in}} = (nN_e)^{1/2}$, we get the $\mathrm{DQE}(n)_m$ as follows

$$\mathrm{DQE}(n)_m \simeq g^2(nN_e)/\{v_g^2g^2(nN_e)^2+(nN_e)g^2+2n(N_d+\sigma_r^2)\}.$$

This expression of the DQE for the multiple read-out is different from that given by Krivanek et al.[2] They fixed the total count which was evenly devided for each read-out. It is noted that $\mathrm{DQE}(n)_m$ is always smaller than $\mathrm{DQE}_m(nN_e)$, i.e. the DQE of the single read-out with the same total incident electrons (nN_e). Thus, there is no way to improve the DQE by the multiple read-out, even when we measure each signal at the incident electrons of N_e for which the DQE is maximum.

3.2 Detection efficiency

The detection limit is essentially determined by the output S/N ratio. However, another important factor is the detection efficiency expressed by the DQE, with which the output S/N ratio is given as $(S/N)_{\mathrm{out}} = \mathrm{DQE}^{1/2}\cdot(S/N)_{\mathrm{in}}$. To understand the behavior of DQE_m or $\mathrm{DQE}(n)_m$, we study each term of its denominator. Fig. 3 shows them as a function of the incident electrons N_e.

In the case of the weak signal, the noises $(N_d+\sigma_r^2)$ dominate other terms, and the DQE is less than one. In this region, $\mathrm{DQE}(n)_m$ is equal to $\mathrm{DQE}_m(N_e)$, i.e. the DQE of each read-out, and thus there is no improvement of the DQE by the multiple read-out. However, the output S/N ratio of the multiple read-out is improved by a factor of $n^{1/2}$, if each signal is larger than the quantization noise of A/D conversion. Neverthless, since $\mathrm{DQE}_m(nN_e) = n\mathrm{DQE}(n)_m$, a single read-out with the prolonged integration time allowed by the dark-current is desired. Then, the S/N ratio is improved by a factor of n. However, it is clear that this system is not adequate to count each electron in contrast to the serial EELS detector with

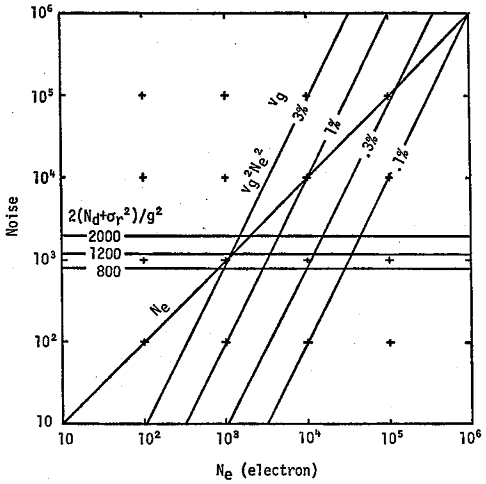

Fig. 3. The strength of each noise component of the signal variance as a function of incident electrons. Each term is normalized by a gain factor.

the function of the pulse-counting.

On the other hand, in the case of the strong signal where $N_e \gg v_g^{-2}$, the noise due to the channel-to-channel gain variation is main term. Then, the DQE is approximately expressed by $\mathrm{DQE}_m \simeq 1/v_g^2 N_e$, which is far less than 1. When the number of incident electrons is increased, the DQE becomes worser and worser. However, $(S/N)_{\mathrm{out}} = N_e^{1/2} \cdot \mathrm{DQE}_m^{1/2} \simeq 1/v_g$, and thus the output S/N ratio is independent of N_e. This means that there is no improvement of the S/N ratio by increasing the incident electrons. When $(N_d + \sigma_r)$ can be neglected, $\mathrm{DQE}(n)_m$ is equal to $\mathrm{DQE}_m(nN_e)$, and thus the output S/N ratio of the both cases are identical. Therefore, the detection limit for the strong signal is restricted by the gain variation.

Between these two regions, the variance is dominated by the noise, $g^2 N_e$ due to the signal itself. Thus, DQE_m and $\mathrm{DQE}(n)_m$ are ideal ($\simeq 1$) here. However, in some cases where the dark current N_d and/or the gain variation v_g is large, there is no such a region at all.

4. DETECTION LIMITS: MDM AND MMF

Isaacson and Johnson[7] discussed two detection limits: MDM (Minimum Detectable Mass) and MMF (Minimum Mass Fraction). The former is the absolute mass which is detectable under a certain condition. The latter is the ratio of the mass of the specific element to the mass of the rest of the specimen within the illuminated volume. For an ideal detector (i.e. DQE=1), they estimated the two detection limits under the experimentally tolerable conditions with the high brightness gun available at that time. Joy and Maher[8] analyzed these two detection limits in the case of the ideal serial detector. However, the actual detector is not ideal. Here we discuss these detection limits based on the previous statistical analysis of this parallel detector.

4.1 Minimum detectable mass

At first, we discuss the MDM. The weakest signal intensity should yield a unit digital output which corresponds to about 20 electrons[2]. Then $DQE_m \simeq 0.025$, and $(S/N)_{out} \simeq 0.7$ for a single read-out. However, the sum of ten read-outs gives $(S/N)_{out}$ which is larger than 2. With the integration times of 100 sec, this gives the lowest counting rate of 0.2 el/sec. Thus, according to Issacson and Johnson[7] the MDM is given by

$$\mathrm{MDM}\ (\delta)=0.2/J\sigma(\delta)\eta,$$

where J is an electron probe current density (in el/sec/cm^2), $\sigma(\delta)$ a scattering cross-section of an energy window δ of each channel, and η a collection efficiency. The MDM given by Isaacson and Johnson is written as $\mathrm{MDM}(\Delta)=10^2/J\sigma(\Delta)\eta$, where $\sigma(\Delta)$ is a scattering cross-section of the energy window Δ. The factor 10^2 is the tolerable counting rate assumed by them. The maximum value of the energy window δ of this detector is 2 eV, while the energy window Δ varies with the element: in the case of the K edges, for example, 50 eV for carbon and 200 eV for Ca. Thus, MDM(δ) is better than MDM(Δ) for light elements, and becomes worser than MDM(Δ) for heavy elements.

4.2 Minimum mass fraction

The other detection limit MMF is more important for a practical application of EELS than the MDM, since the signal P from the specific element usually rides on the background B resulting from the inelastic scattering by other elements as shown in Fig. 4. Here, we can use either the height of the spectrum or the

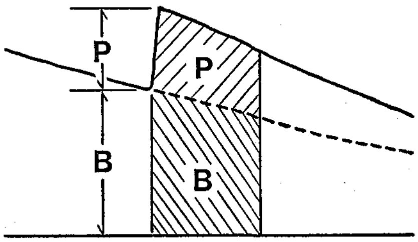

Fig. 4. A typical EELS spectrum showing a peak and background.

integrated intensity to define the signal P and the background B. According to the discussion of Isaacson and Johnson[7], the intensities of the signal P and the background B are given

$$P=J\tau[M\eta_P\sigma_P]\exp(-\rho T\sigma_0'),\ \text{and}$$
$$B=J\tau[M_B\Sigma C_{Bj}\eta_{Bj}\sigma_{Bj}]\exp(-\rho T\sigma_0),$$

respectively. The subscripts P and B_j indicate the element under consideration and the element yielding the background, respectively. C_{Bj} is the mass fractions of the element yielding the background. Two exponential terms represent the artificial absorptions by the aperture. If we neglect the small difference between

σ_0 and σ_0', the MMF is approximated as

$$\mathrm{MMF}=M/M_B \simeq (P/B)\,(\Sigma C_{Bj}\eta_{Bj}\sigma_{Bj}/\eta_P\sigma_P),$$

Thus, the MMF is proportional to the peak to background (P/B) ratio. The second term of this equation can be evaluated for each specimen by assuming a certain optical condition. To estimate the MMF, the lower limit of the P/B ratio should be evaluate for a practical experimental situation. For an ideal detector, the signal and noise are gP and $g\sqrt{B}$, respectively. Thus, Isaacson and Johnson[7] obtained that $P/B=(S/N)_c/\sqrt{B}$ with a critical S/N ratio, $(S/N)_c$, to detect the signal.

However, in the case of the parallel detector, the noise due to the channel-to-channel gain variation dominates the output noise. According to the above statistical analysis, we can assume that $S=gP$ and that $N=\sigma_m \simeq v_g gB$. Thus, we get that $P/B=v_g(S/N)_c$. This equation clearly shows that the P/B ratio is proportional to the relative variance of the channel-to-channel gain variation. With the measured gain variation $v_g \simeq 2\%$ (see below) and $(S/N)_c=2$, we get the P/B ratio of only about 5%.

For the quantitative purpose, we will integrate the spectrum over successive m channels to get the integrated intensity. This will reduce the effect of the channel-to-channel variation by a factor of $\sqrt{m}$. Thus, by integrating the raw spectrum over one hundred channels, we can analyze the element of about 0.5 at.% if we assume the same scattering cross sections.

A better P/B ratio can be obtained by correcting the the channel-to-channel variation, because it does not change during the experiment. We can measure the channel-to-channel gain variation by exposing all the channels to constant illumination. Table 2 shows a result of the correction of the channel-to-channel gain

Table 2. Noise due to channel-to-channel gain variation and its correction.

	A1	A2	Correction
Average	8211.4	82121.7	8203.5
STD (σ)	176.9	1765.4	11.2
Ave/STD	46.4	46.5	730.5

variation. The column A1 shows the statistics of one measurement under constant illumination, while the column A2 shows that of the sum of ten measurements. In both cases, S/N ratio is about 50. This demonstrates that each measurement is dominated by the noise due to the gain variation v_g of $\simeq 2\%$. The last column shows the statistics of the result of A1 corrected by A2. This shows that we can improve the channel-to-channel gain variation by at least one order of magnitude. Other sophisticated procedures proposed by Shumann and Kruit[9] to correct the channel-to-channel gain variation may not be used in general.

The channel-to-channel variation can be further reduced by the multiple read-out of the spectra, which are shifted by one channel successively. This measurement is not difficult by using this PEELS. If we integrate these n spectra, then the noise of the integrated spectrum is reduced by a factor of $\sqrt{n}$. Thus, applying the channel-to-channel gain correction, we can obtain the P/B ratio of 10^{-3} (0.1%) either by one hundred read-outs, or by the intensity integration over one hundred channels.

Extraporating their experiments using a different parallel detector, Shumann and Somlyo[10] estimated the MMF of 83 ppm for Ca embedded in carbon. They used the least square fitting on the second-difference data. Using this parallel EELS detector, it is also expected that for a suitable specimen we can get the MMF of about 10^{-4} (100 ppm) by applying the least square procedure on the data of the P/B ratio of 10^{-3}.

However, it should be noted that these detection limits derived here are based on the detector performance. Thus, these limits can only obtained when the radiation damage does not supercede them.

5. CONCLUSION

Performance of the parallel detector was analyzed based on the statistical model. After some approximation, we get the same expression of the DQE as used by Krivanek et al.[2] Our experiment shows that the relative gain variation v_g of our detector is about 2%, and can be reduced to a value less than one tenth of it by applying the gain correction.

Although this system is not adequate to count each electron, for light elements the minimum detectable mass (MDM) applicable to the parallel detector is smaller than that derived by Isaacson and Johnson[7]. We also estimated the detectable minimum mass fraction (MMF) in the case of the parallel detector for which the noise due to the channel-to-channel gain variation is important. The MMF, which is proprotional to the P/B ratio, is determined by the gain variation v_g. Because of the gain variation, the P/B ratio obtainable by a single raw spectrum is only about 5%. However, by integrating the raw spectrum over one hundred channels, we can analyze the element of about 0.5 at.% if we assume the same scattering cross sections. Moreover, applying the gain correction and the multiple read-out, we can reduce v_g by two order of magnitude. Thus, applying the least square fitting we may detect an element of about 100 ppm embedded in the substrate. This facilitates the elemental analysis of the micro-area by using the electron microscope.

The good detection efficiency and the high quality of data will also facilitate the quantitative analysis of the spectrum, such as EXELFS[11], to investigate the physical and chemical properties of specimens.

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